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ENHANCEMENT OF TETRACHLOROETHYLENE REMOVAL EFFICIENCY BY USING EXTENDED SURFACTANTS

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งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการเพิ่มประสิทธิภาพการชะล้างทรายซึ่งมีเตตระคลอโรเอทิลีนปนเปื้อนอยู่โดยใช้สารลดแรงตึงผิวประเภทขยายโมเลกุลชนิดประจุลบตระกูลอะโฟเทอราซึ่งมีทั้งหมด 7 ชนิด และเพื่อคิดค้นหาสภาวะซึ่งเหมาะสมที่สุดของสารลดแรงตึงผิวประเภทขยายโมเลกุลแต่ละชนิดเพื่อให้สามารถกำจัดเตตระคลอโรเอทิลีนได้ดีที่สุด ในการทดลองนี้ได้ใช้อะโฟเทอราทั้ง 7 ชนิดซึ่งมีความยาวของหางและจำนวนหมู่โพรพิลีนออกไซด์ที่แตกต่างกันร่วมกับโซเดียมไดเฮกซิลซัลโฟซักซิเนตซึ่งเป็นสารลดแรงตึงผิวชนิดประจุลบ เพื่อให้เกิดสารละลายไมโครอิมัลชันกับเตตระคลอโรเอทิลีน และการหาสภาวะซึ่งเหมาะสมที่สุดอยู่บนสมมติฐานว่าเตตระคลอโรเอทิลีนสามารถละลายได้มากที่สุดในไมเซลล์ที่สภาวะไมโครอิมัลชันแบบที่หนึ่งช่วงใกล้การเปลี่ยนวัฏภาคเป็นแบบที่สามซึ่งเรียกว่าซุปเปอร์โซลูบิไลเซชั่น สภาวะซึ่งเหมาะสมดังกล่าวสามารถวัดได้จากการหาค่าแรงตึงผิวและการพิจารณาลักษณะที่ปรากฏของวัฏภาคของสารลดแรงตึงผิวผสมระหว่างอะโฟเทอราแต่ละชนิดและโซเดียมไดเฮกซิลซัลโฟซักซิเนต ในการวิจัยนี้ยังได้ศึกษาผลของความยาวหางและจำนวนหมู่โพรพิลีนออกไซด์ของอะโฟเทอราทั้ง 7 ชนิดที่แตกต่างกัน ซึ่งมีผลต่อความเข้มข้นต่ำสุดในการเกิดไมเซลล์ของสารลดแรงตึงผิวผสม จากการทดลองพบว่าอะโฟเทอราที่มีหางยาวและมีจำนวนหมู่โพรพิลีนออกไซด์มาก จะให้ค่าความเข้มข้นต่ำสุดในการเกิดไมเซลล์ของสารลดแรงตึงผิวผสมต่ำลง สำหรับการศึกษาความสามารถในการละลายของของเตตระคลอโรเอทิลีนในสารลดแรงตึงผิวผสมระหว่างอะโฟเทอราทั้ง 7 ชนิดและโซเดียมไดเฮกซิลซัลโฟซักซิเนตเพื่อเปรียบเทียบผลของความยาวของหางและจำนวนหมู่โพรพิลีนออกไซด์แล้วโดยวิธีแบช ผลจากการทดลองพบว่าอะโฟเทอราที่มีหางยาวและมีจำนวนหมู่โพรพิลีนออกไซด์มาก จะให้ค่าความสามารถในการละลายของสารในไมเซลล์ต่อความสามารถในการละลายของสารในน้ำสูงขึ้น อย่างไรก็ตามผลของตัวแปรทั้งสองค่าข้างต้นมิได้แสดงให้เห็นว่าความสามารถในการละลายของเตตระคลอโรเอทิลีนในสารลดแรงตึงผิวผสมจะมีความสัมพันธ์กันอย่างเป็นเส้นตรง กล่าวคือ หากความยาวหางของอะโฟเทอรามีมากเกินไปค่าความสามารถในการละลายของเตตระคลอโรเอทิลีนกลับลดลงอย่างเห็นได้ชัด จากผลการศึกษาความสามารถในการละลายของเตตระคลอโรเอทิลีนในสารลดแรงตึงผิวผสม พบว่าระบบที่เหมาะสมต่อการละลายของเตตระคลอโรเอทิลีนมีสามระบบ ได้แก่ $C_{12,13}H_{25,27}$-$(PO)_4$–SO_4Na+AMA, $C_{14,15}H_{29,31}$-$(PO)_4$–SO_4Na+AMA และ $C_{14,15}H_{29,31}$-$(PO)_8$–SO_4Na+AMA ซึ่งมีความสามารถในการละลายในปริมาณที่ต่ำ ปานกลาง และสูงตามลำดับ ดังนั้น การทดลองในคอลัมน์จึงใช้ระบบทั้งสามเพื่อศึกษาความสามารถในการกำจัดเตตระคลอโรเอทิลีนโดยวัดจากกลไกการเคลื่อนที่ในแนวดิ่ง ความสามารถในการละลาย และความสามารถในการกำจัดเตตระคลอโรเอทิลีน ผลการทดลองพบว่าสารลดแรงตึงผิวประเภทขยายโมเลกุลสามารถกำจัดเตตระคลอโรเอทิลีนออกได้เป็นปริมาณตั้งแต่ 59 ถึง 83 เปอร์เซนต์ และระบบ $C_{14,15}H_{29,31}$-$(PO)_8$–SO_4Na+AMA สามารถกำจัดเตตระคลอโรเอทิลีนได้ในปริมาณมากที่สุด ซึ่งสอดคล้องกับผลการทดลองหาความสามารถในการละลายของเตตระคลอโรเอทิลีนก่อนหน้าการศึกษาในระบบคอลัมน์

ลายมือชื่อนิสิต Jirussavadee Aumpuch.

สาขาวิชาการจัดการสิ่งแวดล้อม ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก

ปีการศึกษา 2550 ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม

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KEY WORD: EXTENDED SURFACTANT/ MICROEMULSION/ SOLUBILIZATION/ MOBILIZATION/ MICELLE-WATER PARTITIONING COEFFICIENT
JIRUSSAVADEE AUMPUCH: ENHANCEMENT OF TETRACHLOROETHYLENE REMOVAL EFFICIENCY BY USING EXTENDED SURFACTANTS. THESIS ADVISOR: CHANTRA TONGCUMPOU, Ph.D., THESIS PRINCIPAL COADVISOR: PUNJAPORN WESCHAYANWIWAT, Ph.D., 108 pp.

This research aims to introduce seven extended anionic surfactants, Alfoterra series, to enhance the tetrachloroethylene (PCE) removal from contaminated sand, and to investigate the optimum condition of different extended surfactants and electrolyte concentrations that yields the highest PCE removal. Alfoterra surfactants varying alkyl chain length and number of propylene oxide (PO) group in their molecules were used and mixed with sodium dihexyl sulfosuccinate (AMA), anionic surfactant, to form microemulsion solutions with PCE. This study hypothesized that the optimum condition to maximize the solubilization of PCE in micelles occurs at the supersolubilization region in the type I microemulsion. The supersolubilization condition for microemulsion of each Alfoterra mixed with AMA was obtained by measuring interfacial tension incorporated with an observation of an aqueous phase appearance. The critical micelle concentrations (CMC) of mixed Alfoterra surfactants with AMA were determined and found that the longer the Alfoterra chain length or the higher the number of PO group, the lower the CMC. The solubilization study of the seven systems of Alfoterra mixed with AMA was carried out in batch experiments. The results showed that the longer the chain length or the higher the number of PO groups in Alfoterra gives the higher micelle-water partitioning coefficient (K_m) indicating that the PCE solubilization is higher. However, the effects of both factors are not linearly correlated, especially for the very long alkyl chain length, the PCE solubilization is remarkably reduced. From the solubilization study result, the three surfactant systems were selected for column study based on the solubilization capacity for PCE as low, medium, and high namely; $C_{12,13}H_{25,27}$-$(PO)_4SO_4Na$+AMA, $C_{14,15}H_{29,31}$-$(PO)_4SO_4Na$+AMA, and $C_{14,15}H_{29,31}$-$(PO)_8SO_4Na$+AMA, respectively. The total removal of PCE in the column using three surfactant systems was illustrated and the removal mechanism was distinguished as mobilization and solubilization. The results revealed that PCE can be removed from contaminated sand in the range of 59-83%. As expected, the system of $C_{14,15}H_{29,31}$-$(PO)_8SO_4Na$+AMA, which yields the highest solubilization in batch experiments, gives the highest PCE removal by solubilization mechanism.

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LISTS OF ABBREVIATIONS

%w/w	Percent weight by weight
°C	Degree celsius
μL	Microliter
μm	Micrometer
μM	Micromolar
1,2-DCE	1,2-Dichloroethene
Alfoterra	Branch alkyl propyloxylated sulfate
AMA	Sodium dihexyl sulfosuccinate or Aerosal-MA
AOT	Sodium dioctyl sulfosuccinate or Aerosal-OT
$CaCl_2$	Calcium chloride
CMC	Critical micelle concentration
DNAPL	Dense non-aqueous phase liquid
Dowfax	monoalkyl diphenyloxide disulfonates
EACN	Equivalent alkane carbon number
EO	Ethylene oxide group or ethoxylate group
GC-HS	Gas chromatography couple with headspace autosample
HLB	Hydrophile-lipophile balance
IFT	Interfacial tension
IPA	Isopropyl alcohol
K_m	Micelle-water partitioning coefficient
K_{ow}	Octanol-water partitioning coefficient
L	Liter
mg	Milligram
mg/kg	Milligram per kilogram
mg/L	Milligram per liter
mL	Milliliter
mM	Millimolar
mN/m	Millinewton per meter
MSR	Molar solubilization ratio
MW	Molecular weight

NaCl	Sodium chloride
NAPL	Non-aqueous phase liquid
nm	Nanometer
PCE	Tetrachloroethylene or Perchloroethylene
PO	Propylene oxide group or propoxylate group
POE	Polyoxyethylene
ppb	Part per billion
ppm	Part per million
PV	Pore volume
RSD	Relative standard deviation
SDS	Sodium dodecyl sulfate
SEAR	Surfactant enhanced aquifer remediation
SMDNS	Sodium mono- and dimethyl naphthalene sulfonate
SNS	Sodium naphthalene sulfonate
SP	Solubilization parameter
Span 80	Sorbitan monooleate
TCE	Trichloroethylene
Tergitol NP-15	Nonyl phenol ethoxylate
T-MAZ	Ethoxylated sorbital ester
Tween 20	Polyoxyethylene sorbitan monolaurate
Tween 60	Polyoxyethylene sorbitan monostearate
Tween 80	Polyoxyethylene sorbitan monooleate
V	Volume
Witconol 2722	polyoxyethylene (20) sorbitan monooleate

CHAPTER I

INTRODUCTION

1.1 Introduction

Tetrachloroethylene or perchloroethylene (PCE) is a colorless man-made liquid solvent widely used for dry cleaning and grease removal from metal surfaces. PCE structure is shown in Figure 1.1. For household applications, it may be found in paint removers, furniture strippers, water repellents, and adhesives. Since it has been widely used in both industry and household, chlorinated solvents are the most common groundwater contaminants (National Research Council, 1997, and Bedient et. al., 1999). PCE is a nonflammable liquid at room temperature. It evaporates easily to the atmosphere and produces an ether-like odor. PCE is denser than water (density = 1.62 g/cm^3) and less soluble in water, it is thus referred as a dense non-aqueous phase liquid (DNAPL).

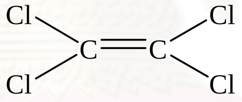

Figure 1.1: PCE structure

PCE can be transported by rainfall into subsurface and water bodies where it can seep through the ground and reaches groundwater. Being a DNAPL, once PCE spill, its plume goes downward direction from the original spot and hence contaminates to groundwater below water table (see Figure 1.2). PCE can persist in soil for many decades and presents a long term threat to groundwater quality because of these following characteristics: 1) low viscosity which enable to invade into the subsurface; 2) high volatilities which enable to contaminate the vadose zone; 3) low absolute solubility which limit the pump and treat method; 4) high solubility with respect to drinking water standards; and 5) low biodegradability (Pankow and Cherry, 1996). The by-products of PCE degradation are trichloroethylene, cis-, trans-dichloroethylene, vinyl chloride, ethylene, and ethane (www.cpge.utexas.edu). Due to its toxicity, PCE can be considered as a non-biodegradable substance.

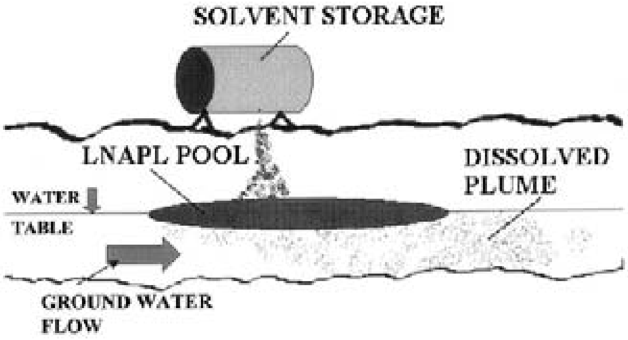

Figure 1.2: Contamination site by a dense non-aqueous phase liquid (DNAPL). Adapted from Harwell et al., 1999.

Like other chlorinated hydrocarbons, PCE can cause dizziness, headache, sleepiness, confusion, nausea, difficulty in speaking and walking, unconsciousness, and death. After repeated skin contact, PCE may dissolve fats from the skin, resulting in a severe skin irritation in working people who have been exposed to PCE at high concentration. PCE may cause liver and kidney cancer. Therefore, the International Agency for Research on Cancer has classified PCE as a Group 2A carcinogen, which means that it is probably carcinogenic to humans. Also, The U.S. Environmental Protection Agency (EPA) presents the data regarding the potential cancer-causing effects of PCE. The U.S. Department of Health and Human Services has determined that PCE may be considered as a carcinogenic substance. So, as to protect public health and the environment, the EPA has established a drinking water standard for a safe drinking water that it should have PCE not more than 5 parts per billion (ppb). For the ambient air quality, the EPA has established the guideline of an annual average concentration of PCE that should not exceed 0.003 ppb (www.epa.gov).

For the problem of PCE in the United States, PCE has been found in at least 771 of the 1,430 National Priorities sites identified by the USEPA (www.cpge.utexas.edu). Exposure to PCE alone typically does not mean a person will experience adverse health effects. Many factors determine whether people experience adverse health effects due to chemical exposure such as dose, the duration of exposure, exposures to other chemicals in a lifetime, and overall state of health. Furthermore, tetrachloroethylene was on the first priority substances list under the Canadian Environmental Protection Act (CEPA), announced in 1989 (www.ns.ec.gc.ca). The federal government is currently developing controls to reduce environmental exposure of PCE. In Thailand, PCE is in the Hazardous Substance Act of B.E. 2535 (1992). In addition, the Pollution Control Department is going to set the standard for PCE because some experimental data show that it obviously cause some type of cancer.

Due to problems of PCE mentioned above, the subsurface contamination by PCE is gaining more environmental concern. The basic problem of PCE arises from the fact that PCE is trapped by capillary force within soil pores because of the high oil-water interfacial tension (IFT) (Shiau et al., 1995). One basic remediation method to remove PCE from the contaminated site is the pump-and-treat (Haley et al., 1991; and Palmer and fish, 1992). The conventional remediation method of pump and treat involves a pumping of water through the contaminated site followed by a treatment of effluent stream above ground by air stripping, steam stripping, or activated carbon filtration (Dwarakanath et al., 1999). However, it is ineffective because it requires hundreds to thousands pore volumes of water to flush trapped-oil-like PCE with water due to a fact that PCE is almost immiscible with water (solubility = 150 ppm) and denser than water. Another popular technique to remove PCE from the contaminated site is to use surfactant, by so called “Surfactant Enhanced Aquifer Remediation (SEAR)” technique, for increasing the solubility of the NAPL constituents in surfactant aqueous solution, which is especially attractive for several reasons (Fauntain et al., 1991; Pennel et al., 1996; Sabatini et al., 1995, and 1997). First, surfactants have specific properties on decreasing IFT between oil and water as well as oil and subsurface, hence, PCE that are trapped in the porous media can be detached and flushed out with surfactant aqueous solution. Second, there are numerous kinds of surfactants commercially available, which are non-toxic to mammals and they are well-established biodegradability. Ultimately, surfactants are known to be an effective cleaning agent even at low concentration (Harwell et al., 1999).

Due to the fact that surfactant is an amphiphile molecule containing both hydrophilic (polar) and lipophilic (non-polar) parts, a non-polar PCE tends to partition into the surfactant micelles. The structure of surfactant is shown in Figure 1.3.

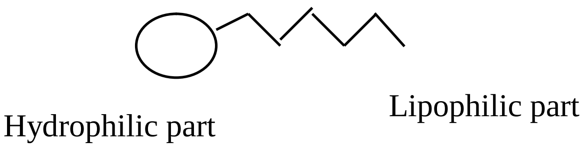

Figure 1.3: Surfactant structure

If an aqueous surfactant is flushed into the PCE contaminated site, PCE will solubilize to the lipophilic part of the surfactant and then be removed along with flushing water. Furthermore, Alfoterra, the extended anionic surfactant used in this study is expected to be able to enhance the PCE solubilization since it contains propylene oxide (PO) groups that can provide a smoother transition between hydrophilic and lipophilic interface of surfactant. As a result, a suitable environment for solubilizing lipophilic molecules like PCE is created.

1.2 Objectives

The ultimate objective of this study is to introduce the extended surfactants, Alfoterras, to enhance the PCE removal from contaminated subsurface and to investigate the optimum condition of different extended surfactant systems and electrolyte concentrations that yields the highest PCE removal. The specific objectives are as follows:

1. To compare the effects of alkyl chain length and number of PO groups in Alfoterra molecule on PCE solubilization.
2. To study the solubilization of PCE in microemulsion system formed by the extended surfactants.
3. To select the suitable extended surfactant systems to remove PCE from contaminated sand in column study.

1.3 Hypotheses

The extended surfactants are expected to enhance PCE removal as compared to the conventional surfactants due to their specific structure that contains an internal linker, propylene oxide or PO group. The effects of different structure of extended surfactant are hypothesized as follows:

1. The higher the PO group in surfactant structure, the more the solubilization of PCE is obtained. As Alfoterra appears in oil phase, it will promote the orientation of oil molecules because it serves as a link between oil molecules and surfactant tail. Since extended surfactant behaves like lipophilic linker, it will increase lipophilic portion of surfactant. Consequently, PCE can solubilize more. The mechanism of lipophilic linker is shown in Figure 1.4.

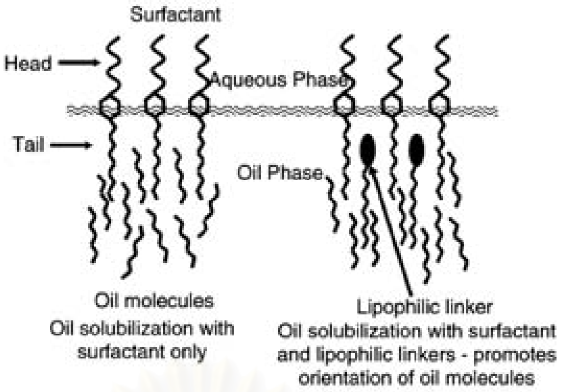

Figure 1.4: Orientation of lipophilic linker with surfactant molecules. Adapted from Graciaa et al., 1993.

The longer the alkyl chain length of surfactant, the higher the solubilization of PCE is achieved. Since PCE is a non-polar organic molecule, it easily solubilizes in the surfactant micelles that have lipophilic environment.

1.4 Scope of study

1. Phase behavior study

The optimal salinity and interfacial tension for each Alfoterra serie mixed with AMA were investigated. The condition obtained from the phase study was then used as a starting point in the next parts of the study.

2. CMC determination

The CMC of each surfactant system (various types of Alfoterra mixed with AMA) in the presence of NaCl at their respective optimum salinity concentration obtained from phase behavior study was determined.

3. Solubilization study

The solubilization of PCE in different type of Alfoterra mixed with AMA at optimal salinity was studied. The molar solubilization parameter (MSR) and micelle-water partition coefficient (K_m) were investigated.

4. Column study

The percentage of PCE removal by flushing the contaminated sand packed in the column with the selected surfactant solution obtained from solubilization experiment was investigated. In this work, silica (Ottawa) sand was used to pack in column.

CHAPTER II

THEORITICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Surfactant

Surfactant, a contraction of a term: surface active agent, is a substance consisting of a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail in its molecule structure. Due to its amphiphilic structure, a surfactant can greatly reduce interfacial tension between water and oil, even through the surfactant presents in very low concentration (Harwell et al., 1999).

There are four basic types of surfactant which are classified based on the charge of their hydrophilic head group.

1. Anionic surfactant: these surfactants have negatively charged at their hydrophilic head. They are widely used as detergents and household cleaners. The examples of anionic surfactants are alkyl sulfates, alkyl sulfonates, and alkyl phosphates.
2. Cationic surfactant: these surfactants have positively charged at their hydrophilic head. They are commonly used in fabric softener, and laundry detergents. The examples of cationic surfactants are ethoxylated fatty amines.
3. Zwitterionic surfactant: these surfactants have both positively and negatively charged at their hydrophilic head depending upon pH. Their uses are quite limit such as in skin-care products. The examples of zwitterionic surfactants are amine oxide, ammonium carboxylate, and ammonium sulfate.
4. Nonionic surfactant: these surfactants have no charge at their hydrophilic head. They are widely used in foods and drinks, and pharmaceutical products. The examples of nonionic surfactants are alkylphenol ethoxylates, and alcohol ethoxylates.

2.2 Micelle and critical micelle concentration

Surfactant is able to assemble in various forms of aggregation depended on the surfactant concentrations and the presence of additives such as electrolyte and organic solute in solution. When the surfactants are added in a system, it produces a higher free energy. So, the system is not stable and free energy needs to be decreased. As a consequence, at low concentration of surfactant, surfactant monomer adsorbs at the surface of the solution in order to decrease the free energy of the system because both portions of surfactant molecule can be in a preferred phase (Shiau et al., 1995). When the surface of solution is occupied, the only way to decline the free energy is to form a surfactant cluster called micelle. The surfactant concentration that first micelle occurs is called "critical micelle concentration", or CMC. Formation of micelle is spontaneously occurred (Sabatini et al., 2000). This unique property of surfactant attributes to solubilization capacity of surfactants resulted to a dramatically enhance of an aqueous solubility of hydrophobic organic compounds at surfactant concentrations above the CMC (Saito and Shinoda, 1967; and Kile and Chiou, 1989).

The CMC value is a property of surfactant that also depends upon a number of other factors including temperature, pressure, and the presence of additives. Once a micelle form, its inner property can facilitate oil or solubilizate to solubilize in different regions according to the oil properties. There are 3 regions in a micelle: inner hydrophobic core, palisade layer and polar surface region as shown in Figure 2.1 (Jaynes, 1985).

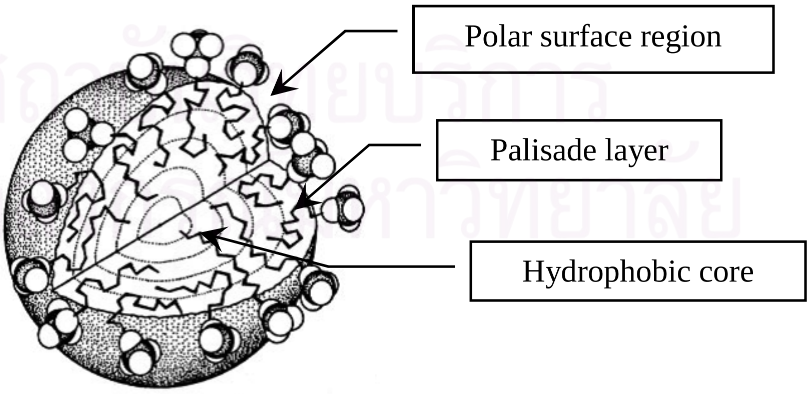

Figure 2.1: Structure of micelle

The hydrophobic core is located at the center of the micelles, non-polar oils are preferable to be solubilized in this region due to a strong affinity between the hydrophobic oil and non-polar environment provided by surfactant tail. The palisade layer which locates between the surfactant head and tail providing a mixed environment of hydrophobic and hydrophilic influenced by both head and tail of a surfactant, thus semipolar and polar oils are likely to be solubilized in this layer. For the polar surface region or at the head group layer, in general, oils are not preferable to solubilize here (Tadros, 2005).

CMC of a given surfactant can be determined by several methods, the most common and accurate technique is carried out by measuring of surface tension of the surfactant solution at different concentrations, then plot surface tension versus logarithm of surfactant concentration as shown in Figure 2.2 (Yeh et al., 2002). The point at the transition of region 2 to region 3, where the first micelle is formed, is considered as “CMC” of a surfactant at measuring temperature (Rosen, 2004).

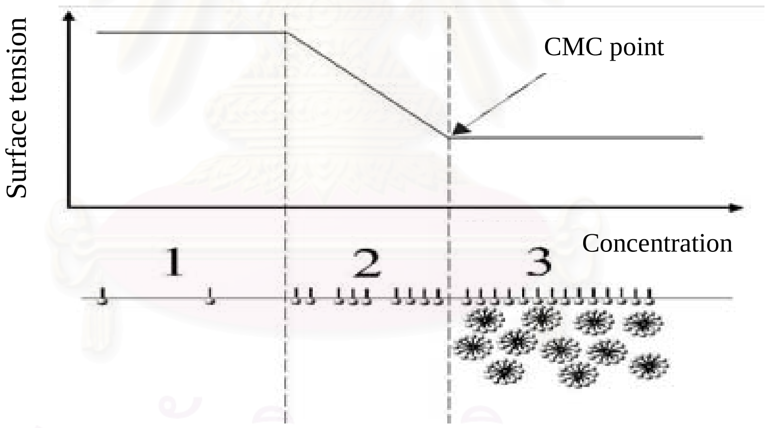

Figure 2.2: Surface tension at different surfactant concentrations

In most cases of surfactant application, especially for oil removal via solubilization mechanism, the surfactant concentrations used are normally higher than its CMC, so the micelles exist and be able to solubilize oil.

These surfactant micelles can uptake or absorb organic pollutants by so called “solubilization” phenomenon (see Figure 2.3). In addition, the longer the hydrophobic chain length of surfactant, the lower the CMC is obtained. Obviously, the higher the micelles presents in aqueous solution, the more organic solute or pollutant is removed and eliminated from the contaminated site as shown in Figure 2.3 (Adamson, 1990; and West and Harwell, 1992).

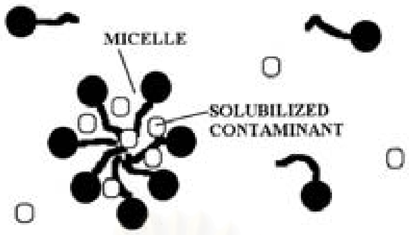

Figure 2.3: Solubilized organic pollutant in surfactant micelle

2.3 Microemulsion phase transition

Microemulsion is a system containing water, oil, and surfactant, which is thermodynamically stable (Sabatini et al., 2000). The differences between emulsion and microemulsion are their particle size (~10-100 nm for microemulsion) and stability. The important properties of microemulsion are having ultra-low IFT, large surface area, capacity to solubilize both aqueous and oil compounds (Paul and Moulik et al., 2001). Regarding these properties, microemulsions are considered as an effective method to enhance oil remediation (Holmberg et al., 2003).

Microemulsion can be formed and transitioned among four basic types: Winsor type I, Winsor type III, Winsor type II, and Winsor type IV, depending on the hydrophile-lipophile balance (HLB) of the system (Childs et al., 2004; and Rosen et al., 2004). If the surfactant micelles dissolve in the aqueous phase (oil solubilized in aqueous micelle), the normal micelles (surfactant aggregates having hydrophobic interior and hydrophilic exterior) are formed. This is called a Winsor type I microemulsion. When the HLB of the system is reduced (i.e., by increasing salt for anionic surfactant system or decreasing temperature for non-ionic surfactant), an aqueous surfactant phase and an oil phase will reduce their interaction force at the interface, resulting in an occurrence of the least curvature surfactant aggregation known as bicontinuous structure. The Winsor Type III microemulsion, or middle phase microemulsion is formed. In this region, the highest solubilization and the lowest interfacial tension are obtained. Once the HLB is further reduced, the normal micelles break up, move into oil phase and transform into reverse micelles (water solubilized in reverse micelle). This is called a Winsor type II microemulsion.

Microemulsion phase behavior so called Winsor diagram is shown in Figure 2.4 (Shiau et al., 1994; and Sabatini et al., 1996)

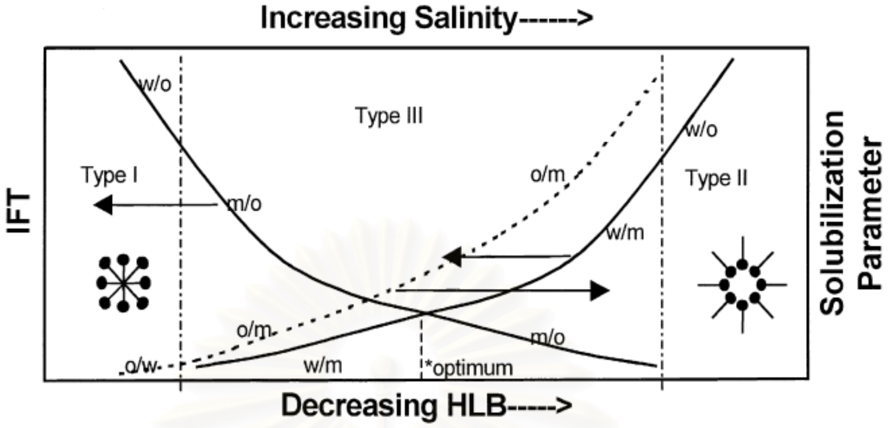

Figure 2.4: Winsor phase diagram adapted from Sabatini et al., 2000.

At specific condition, another type of microemulsion, which is called Winsor type IV, can be generated. The Winsor type IV is a single phase system that water, oil, and surfactant combine together into one phase, which usually occurs at very high surfactant concentration (Bourrel and Chambu, 1983; and Acosta et al., 2004).

Form the Winsor phase diagram, at the region closed to a boundary between Winsor type I and type III, the solubilization of oil is relatively high and interfacial tension is considerably low. Several applications including surfactant enhanced remediation of Dense Nonaqueous Phase Liquid (DNAPL) are preferable to operate at this region, which is so called “supersolubilization region” (Pennel et al., 1996; and Wu et al., 2000). In this region, micelles are most swollen because of the highest oil solubilization (West et al., 1992).

The possibility to form microemulsion with given oil is mainly based on the compatibility of surfactant and oil. In most cases, mixed surfactants are required, especially for oil with complicated structure, for instance, PCE, motor oil, vegetable oil, etc. In addition, linkers or co-solvents such as alcohols are also employed. Sodium dihexylsulfosuccinate (AMA) and sodium dioctylsulfosuccinate (AOT) are the most common anionic surfactants used for microemulsion formation. They have been chosen due to their high compatibility with soil media, low potential to form gel or liquid crystal phase, very fast solubilization rate, low toxicity, and especially being food grade additives (Mayer et al., 1999; and Dwarakanath and Pope, 2000).

2.4 Winsor R-ratio

The microemulsion transition is governed by the hydrophilicity and lipophilicity of the system as described by the Winsor R-ratio as followed (Winsor, 1948, 1954).

$$R = \frac{A_{SO-NET}}{A_{SW-NET}} = \frac{A_{SO} - A_{OO} - A_{LL}}{A_{SW} - A_{WW} - A_{HH}}$$

where

$A_{SO\text{-}NET}$: the net interaction between the surfactant and oil

$A_{SW\text{-}NET}$: the net interaction between the surfactant and water

A_{SO} : the interaction between the surfactant and oil

A_{SW} : the interaction between the surfactant and water

A_{OO} : the interaction energy among oil molecules

A_{LL} : the interaction among the tails of the surfactant molecules

A_{WW} : the interaction energy among the water molecules

A_{HH} : the interaction among the surfactant heads

Hydrophilic interaction

- Increased electrolyte concentration will make A_{HH} larger for ionic surfactant because of repulsive force.
- For nonionic surfactant, being less hydrophilic will cause a decrease in the interaction with water thus, leading to the A_{SW} reduction.

Lipophilic interaction

- Increased length of lipophile will cause an increase in A_{LL}.

The optimum formulation is obtained when the net interactions $A_{SW\text{-}NET}$ and $A_{SO\text{-}NET}$ are equal (R=1) and will be occurred in the region of Winsor type III or middle phase microemulsion. Also, the solubilization increases and the IFT decreases when each of these interactions is higher but equal. The addition of electrolyte in surfactant solution is used to suppress the double layer around the anionic head group of surfactant, thus reducing A_{SW} and $A_{SW\text{-}NET}$. As a consequence, electrolyte addition is needed since normally $A_{SW\text{-}NET}$ is larger, due to high surfactant solubilization in water, than $A_{SO\text{-}NET}$ (Witthayapanyanon et al., 2006).

2.5 Linker

Linker molecules are amphiphiles which are either lipophilic or hydrophilic. Amphiphiles also help eliminating the formation of undesirable gel (Child et al., 2004). Augmentation of the interaction between surfactant and oil phases, or between surfactant and water phases can be accomplished by adding lipophilic linkers, and hydrophilic linkers, respectively. Lipophilic linkers can increase the interaction between oil molecule and surfactant tail since they orientate along the surfactant tails and promote orientation of oil molecules into surfactants. The solubilization capacity linearly increases with increasing concentration and lengthening alkyl chain length of lipophilic linker (Graciaa et al., 1993; and Uchiyama et al., 2000). An example of lipophilic linker is long chain alcohols (> 9 carbons). Nonetheless, at certain concentration of lipophilic linkers, the solubilization of oil molecules remains stable (Salager et al., 1998) due to the saturation of lipophilic linkers in the surfactant micelles (Uchiyama et al., 2000; and Sabatini et al., 2003). In order to solve this problem, adding hydrophilic linkers is suggested. The hydrophilic linkers open up a space on the oil side of the interface where the lipophilic linker segregates. Combining both linkers can increase oil solubilization for several folds (Sabatini et al., 2003). The examples of hydrophilic linkers are sodium naphthalene sulfonate (SNS), sodium mono– and dimethyl-naphthalene sulfonate (SMDNS). However, there are some limitations of using linker. Since not all linkers aggregate near the interface, some partitions between different phases (Sabatini et al., 2003). For instance, lipophilic linker molecules may solubilize in oil phase rather than partition near hydrophobic tail of surfactant. Consequently, it does not help increasing oil solubilization. In order to offset this partitioning effect, one alternative is to use the extended surfactant.

2.6 Extended surfactant

Extended surfactants are a new generation of surfactants that have been recently produced to enhance their ability to solubilize hydrophobic oils. In the molecule of extended surfactant, the hydrocarbon tail is ″extended″ by a number of ethoxylate groups (EO) and/or propoxylate groups (PO) inserted between the surfactant head and the hydrocarbon tail as shown in Figure 2.5. Due to the unique molecular structure, the surfactant is stretched out further into both oil and water phases. These surfactants provide a smoother transition between the hydrophilic and hydrophobic interface resulting in a more suitable environment for solubilizing hydrophilic and lipophilic molecules (Witthayapanyanon et al., 2006).

Besides from specific structure of extended surfactant that would enhance the oil solubilization, being an anionic surfactant is also desirable since HLB can be adjusted easily as compared to the nonionic surfactants (Dwarakanath et al., 1999).

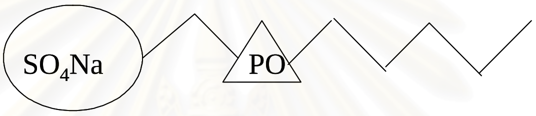

Figure 2.5: Extended surfactant structure

2.7 Determination of oil solubilization

As mentioned earlier, the solubilization is a key performance of surfactant aggregates particularly for environmental application where these surfactant solutions can be applied to remove pollutants from environmental media. Thus, investigation of a capability of surfactant systems to enhance solubilization of studied oils is a crucial aspect. Since the solubilization of organic compounds results from the affinity between organic compounds to surfactant that governing the partitioning of compounds into hydrophobic core of surfactant micelles, a selection of suitable surfactants is important if one wants to enhance the oil solubilization capacity of surfactant. To analyze oil solubilization capacity in any surfactant systems, a technique called the molar solubilization ratio (MSR) has been purposed and widely used (Edwards et al., 1991; and West, 1992). Once the MSR is obtained, the micelle-water partitioning coefficient (K_m) can be calculated and these two parameters are used to describe the solubilization capacity of a surfactant system for given oil.

The molar solubilization ratio or moles of contaminant per mole of surfactant is determined from a slope of the graph plotted between contaminant solubility (y-axis) and surfactant concentration (x-axis) above its CMC (Pennel et al., 1997).

$$MSR = \frac{(S - S_{CMC})}{(C_S - CMC)} \qquad \text{……..… (1)}$$

Where S is the aqueous plus micellar phase solubility (apparent solubility) of solute at a particular surfactant concentration greater than the CMC; and C_S is the surfactant concentration at which S is evaluated; S_{CMC} is the apparent solubility of PCE at the CMC (Zhu and Feng, 2003).

The micelle-water partitioning coefficient, $K_{m,}$ is the molar ratio (distribution) of contaminant in the micelle phase divided by the molar ratio of contaminant in aqueous phase. It can be quantified by the below equation (Edwards et al., 1991; Shiau et al., 1995).

$$K_m = \frac{55.5MSR}{S_{CMC}\,(1 + MSR)} \qquad \text{……..… (2)}$$

From the study of Shiau et al. (1994), S_{CMC} of PCE in the surfactant system was found to be 4.86×10^{-4} M. The S_{CMC} in some studies was assumed to be equal to the equilibrium concentration of the solute in water alone or water solubility of that solute (Fuangswasdi et al., 2006).

2.8 Surfactant enhanced aquifer remediation (SEAR)

Due to the fact that micelle formation reduces the interfacial tension (IFT), the surfactant enhanced aquifer remediation (SEAR) has been introduced for subsurface remediation (Child et al., 2004). In order to decrease the IFT of the system, the hydrophilic part of surfactant will bind with water and lipophilic part of surfactant will bind with oil molecule. In addition, surfactant also helps providing the hydrophobic environment for non-aqueous phase liquid (NAPL) to solubilize into the surfactant micelles.

For the DNAPL like PCE, the vertical migration associated with mobilization is a major concern since the detached DNAPL can sink to uncontaminated groundwater since it is denser than water. The microemulsion approach was proposed and operated for PCE removal at “supersolubilization” region (Pennel et al., 1996; and Acosta et al., 2002). In this region, micelles are most swollen with greatest potential to solubilize PCE (West et al., 1992). Furthermore, an addition of neutral electrolyte to ionic surfactant tends to increase the solubilization of nonpolar contaminant due to a closer packing of surfactant heads. Another advantage of adding electrolyte is to decrease the CMC of ionic surfactant since the electrostatic repulsion is screened out. Nevertheless, an introduction of high salt concentration is not a desirable method, as a remediation of brine contamination is also a difficult problem (Shiau et al., 1995). Therefore, in this research, altering the HLB by mixed binary surfactants with different HLB was suggested since PCE showed the maximum solubility at the HLB of 14 (Pennel et al., 1997).

Mixed surfactant systems are quite common in surfactant technology applications because these mixtures frequently outperform the surface active behavior as compared to pure surfactant systems (Sabatini et al., 2003). Molecular structure of surfactant is one essential characteristic for surfactant selection. An increase in the hydrophobic chain length of surfactant can increase the solubility of surfactant in oil phase. Conversely, its solubility in water decreases.

2.9 Previous studies on solubilization and PCE removal

Shiau et al. (1995) compared the efficiency of solubilization (contaminant partitioning into surfactant, the oil-like core micelle, thereby increasing the apparent aqueous solubility of contaminant) and microemulsification (formation of Winsor type III or middle phase microemulsion) on PCE, TCE, and 1,2-DCE. The results showed that the removal efficiency of microemulsification (5.0wt% AOT and SMDNS) gave higher efficiency than solubilization (6.5wt% T-MAZ60), which is more than 99% in 3 pore volumes in the former case and approximately 85% in 10 pore volumes in the latter case. Moreover, they also stated that K_m varies depended more on varying types of contaminants for a given surfactant than varying type of surfactants for a given contaminant.

Harwell et al. (1999) compared the efficiency of 70% PCE removal between water and the surfactant solution. Sodium dodecylbenzene sulfonate (SDBS), commonly used in laundry detergent, requires the lowest pore volumes of 35 to flush, followed by ethoxylated sorbital ester (T-MAZ 20) of another 50 pore volumes. Water alone, on the other hand, requires 1,300 pore volumes. Moreover, they found that only 0.7 pore volumes of a Winsor Type III or middle phase microemulsion (T-MAZ 80 with Aerosol-OT) can remove up to 70% of PCE.

Graciaa et al. (1993) observed the effect of lipophilic linkers in microemulsion systems. They believed that lipophilic linker distributes in the oil phase, orientates along with the tail of surfactant, and supports the orientation of oil molecules into surfactant micelles. Lipophilic linkers thus serve as a link between oil molecules and the surfactant tails. Moreover, they proposed that alcohols with two to four carbons showed a cosolvent effect that helps decreasing the surface-surface interaction. Likewise, they proposed that alcohols with four to nine carbons are considered as cosurfactants and for the ones with ten or more carbons are considered as lipophilic linker molecules. With different alkyl chain length in alcohols, the solubilization enhancement was proportion to the concentration of alcohol and the number of carbons in its molecule.

Sabatini et al. (2003) examined the use of linker molecules in order to increase the solubilization capacity of surfactant for PCE. In this experiment, sodium dihexyl sulfosuccinate (AMA) was used as a surfactant coupled with dodecanol and oleyl alcohol as lipophilic linkers. The solubilization capacity was measured by the solubilization parameter (SP). With an increase of alcohol concentration and alkyl chain length, the solubilization capacity proportionally increases. They also found that if the concentration of the lipophilic linker reaches one certain point, the solubilization enhancement reaches a plateau. They believed that the plateau region results from the saturation of the lipophilic linker near the surfactant molecules. As the lipophilic linker becomes saturated at high concentration, they also proposed the use of hydrophilic linker molecules to co-adsorb with the surface at the oil-water interface. Sodium mono- and dimethyl-naphthalein sulfonate (SMDNS) was used in the experiment. According to the data, whereas lipophilic linker fits in between surfactant molecules, the hydrophilic linker opens a space on the oil side of the interface where the lipophilic linker segregates.

Acosta et al. (2003) observed that high concentration of electrolyte (~10% NaCl) promotes the precipitation of surfactant. Addition of linker into surfactant system promotes a phase separation of solution containing surfactant and linkers. Although phase separation may disappear with the addition of oil to form microemulsion phase, it is inconvenient for subsurface remediation where it is desired to inject a single-phase isotropic surfactant solution.

Dwarakanath et al. (1999) described the advantage of using anionic surfactant over nonionic surfactant. As the salinity can be adjusted inexpensively for anionic surfactant, it is very practical to control a surfactant flood and improve the solubilization capacity. Unlike anionic surfactant, the oil solubilization capacity of nonionic surfactant can be adjusted only by temperature which hardly done in the field. The other point is that the surfactant solution containing polymer promotes more uniform transport of the surfactant solution and thus increase the contact with the trapped DNAPL. Therefore, adding polymer in the surfactant solution will increase the efficiency of the flushing process. Moreover, liquid crystal may be eradicated when adding sufficient amounts of light alcohols and increasing the temperature. The results showed that more than 99% of PCE was removed as a result of surfactant flooding in the soil column.

Witthayapanyanon et al. (2006) formulated the ultra low interfacial tension systems using extended surfactants. The two classes of extended surfactant; sodium alkyl polypropyleneoxide sulfate ($R-(PO)_x-SO_4Na$), and sodium alkyl polypropyleneoxide polyethyleneoxide sulfate ($R-(PO)_y-(EO)_z-SO_4Na$) were used in their study including $C_{14-15}-(PO)_8-SO_4Na$ and $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$. Although the molecular structures of these surfactants are different, they have similar HLB values. The main difference between the two surfactants is the addition of PO and EO groups. The results showed that extended surfactant systems have lower critical micelle concentrations (CMC) than conventional surfactants. Moreover, the extended surfactant provides an ultra low interfacial tensions (IFT) with highly hydrophobic oils such as vegetable oils and petroleum hydrocarbons. They also compared the IFT of extended surfactant with conventional surfactant. The results showed that the extended surfactant system gave IFT value closed to 0.01 mN/m, but for the conventional surfactant AOT, the IFT remains above 1 mN/m for all electrolyte concentrations used in this study. The important finding in this work is the ultralow IFT with triglycerides has been achieved using surfactant concentrations in the range of 0.1 to 1.0 mM without the addition of co-oils and/or alcohol. In addition, they found that all of the extended surfactants have CMC values much lower than conventional C_{12} and C_{14} surfactants. They also observed a decrease in CMC of the extended surfactants as the alkyl chain length increase (130 μM for $C_{12-13}-(PO)_8-$

SO_4Na and 33 µM for $C_{14\text{-}15}$-$(PO)_8$-SO_4Na); this four-fold decrease is similar to a decrease in the conventional C_{12} to C_{14} surfactants.

In this study, an extended surfactant was firstly introduced for PCE removal. We hypothesized that the surfactant systems that provide high PCE solubilization as investigated in the batch experiments would show a high PCE removal efficiency in column study. Seven extended surfactants were used in the solubilization study and the MSR and log K_m of those surfactant systems were compared.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Surfactants

3.1.1.1 Branched alkyl propyloxylated sulfate

Seven types of branched alkyl propyloxylated sulfate (in the trade name of Alfoterra) were used as anionic extended surfactants to compare the efficiency of PCE removal. Alfoterras were donated from Sasol North America Inc. (LA, USA). The properties of Alfoterras are shown in Table 3.1.

Table 3.1: Properties of the extended surfactants

Extended surfactant	Hydrocarbon chain	#PO	% Active	MW (g/mol)
Alkyl-(PO)$_X$-SO$_4$Na				
1. $C_{12,13}H_{25,27}$-(PO)$_4$–SO$_4$Na	12-13	4	32.5	527
2. $C_{12,13}H_{25,27}$-(PO)$_8$–SO$_4$Na	12-13	8	30.7	759
3. $C_{14,15}H_{29,31}$-(PO)$_3$–SO$_4$Na	14-15	3	28.6	497
4. $C_{14,15}H_{29,31}$-(PO)$_4$–SO$_4$Na	14-15	4	34.9	555
5. $C_{14,15}H_{29,31}$-(PO)$_8$–SO$_4$Na	14-15	8	29.5	787
6. $C_{16,17}H_{33,35}$-(PO)$_4$–SO$_4$Na	16-17	4	30.0	583
7. $C_{16,17}H_{33,35}$-(PO)$_7$–SO$_4$Na	16-17	7	30.9	757

PO: Propylene oxide (C_3H_6O)

3.1.1.2 Sodium dihexyl sulfosuccinate

Sodium dihexyl sulfosuccinate (in the trade name of Aerosal MA or AMA), an anionic surfactant, was used to adjust the HLB of the system to reduce the concentration of electrolyte required to induce the microemulsion transition. The AMA with 80% active was purchased from Fluka Company (USA).

3.1.2 Organic pollutant

Tetrachloroethylene or PCE with 95% purity was purchased from Sigma-Aldrich Co. The physical and chemical properties of PCE are shown in Table 3.2 (National Institute for Occupational Safety and Health, 2000).

Table 3.2: The physical and chemical properties of PCE

Formula	$Cl_2C{=}CCl_2$
Molecular weight	166
Vapor pressure (atm) at 25 ºC	0.132
Boiling point (ºC)	120
Melting point (ºC)	-22.7
Water solubility (mg/L)	149
Log K_{ow}	3.40
Density (g/cm^3)	1.62
EACN	2.9
Viscosity (cP)	0.844
Color	colorless

3.1.3 Electrolyte

Sodium chloride (NaCl) was used in this study as electrolyte since it tends not to be easily precipitate with SO_4 functional group in Alfoterra structure as compared to $CaCl_2$. The NaCl (analytical grade) with 99% purity was purchased from Lab-Scan Ltd. (Ireland).

3.1.4 Adsorbent

Ottawa sand or silica sand (20-30 mesh) with low iron was used as the synthetic soil in this study purchased from Fisher Scientific Co., Ltd. (UK).

3.2 Methodology

The experiments were divided into 4 parts. The schematic diagram is shown in Figure 3.1.

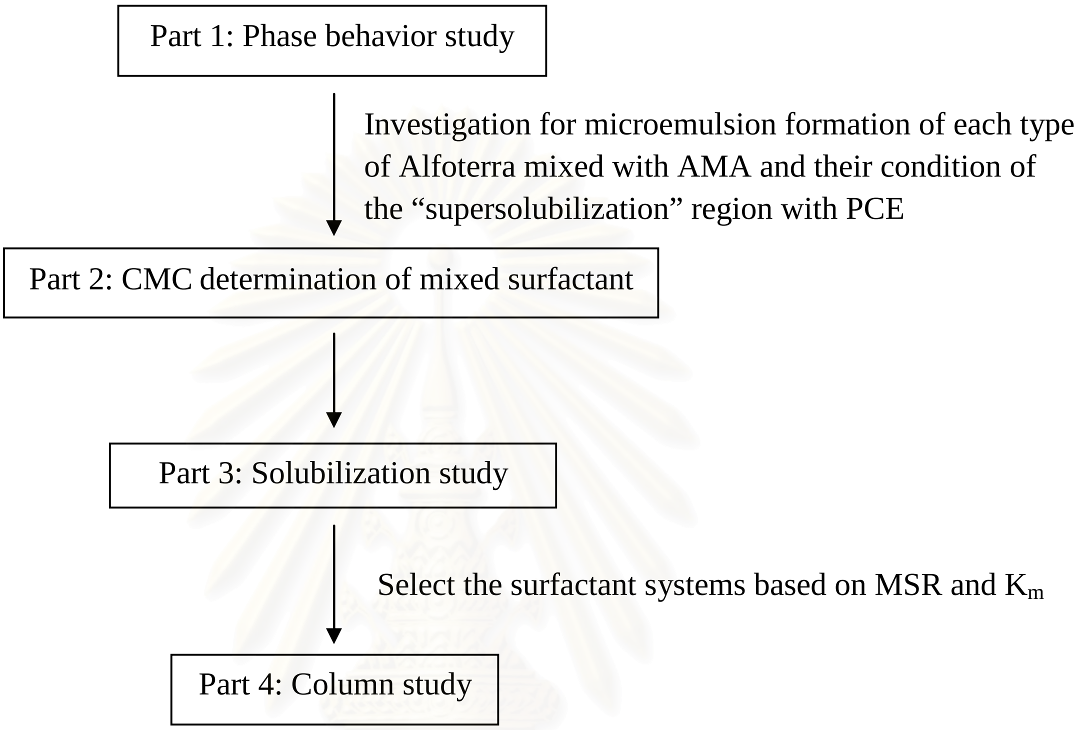

Figure 3.1: Flow chart of this experiment

3.2.1 Phase behavior study

The phase study was conducted with systems of mixed AMA and individual Alfoterra surfactant (mixing ratio = 1:1 by mole). Phase scan was carried out by varying salinity in a system of molar equivalent ratio of surfactant solutions and PCE in order to determine the electrolyte concentration needed for each mixed surfactant system to form the supersolubilization condition. NaCl was added into each vial with different concentration. Each vial was mildly shaken for 2 minutes. To investigate the salinity concentration of the supersolubilization region, only NaCl concentrations were varied in the phase scan. Dynamic IFT was measured by the dataphysics SVT20 spinning drop tensiometer (SVT20, DataPhysics, DataPhysics Instruments GmbH). A graph between IFT (y-axis) versus electrolyte concentration (x-axis) was plotted. The suitable electrolyte concentration to form “supersolubilization” region was justified by a decreasing of IFT value in the graph incorporated with a consideration on the appearance of an aqueous phase. The aqueous phase at the supersolubilization region is oil in water microemulsion, where the NAPL solubilization in the surfactant micelles is maximized that generally shows as a milky solution. The preliminary study showed that the system of mixed Alfoterra and AMA was able to form microemulsion with PCE.

3.2.2 CMC determination

The CMC of each mixed surfactant system; Alfoterra mixed with AMA system was determined by preparing each system at different total surfactant concentrations with no NaCl concentration. Then, the surface tension of each surfactant solution was measured by Tensiometer (DCAT11, DataPhysics, DataPhysics Instruments GmbH) using a platinum plate which is known as the Wilhelmy plate method at 28°C (Sánchez et al., 1998). The CMC of each system can be obtained from the plot between surface tension versus logarithm of total concentration of mixed surfactant. A sharp change of the plot indicates the CMC of the mixed surfactants.

3.2.3 Solubilization study

The solubilization of oil in surfactant solution was determined by technique called Molar Solubilization Ratio (MSR). The molar solubilization ratio or moles of contaminant per mole of surfactant is determined from a slope of the graph plotted between contaminant solubility (y-axis) and surfactant concentration (x-axis) above its CMC (Pennel et al., 1997). After MSR of each mixed surfactant system was obtained, the micelle-water partitioning coefficient, or K_m, of each Alfoterra mixed with AMA was calculated. The micelle-water partitioning coefficient is the molar ratio (distribution) of contaminant in the micellar phase divided by the molar ratio of contaminant in an aqueous phase. This parameter is also used to indicate the solubilization of oil in surfactant solution. It can be quantified by the below equation (Edwards et al., 1991; Shiau et al., 1995).

$$K_m = \frac{55.5\text{MSR}}{S_{CMC}\,(1 + \text{MSR})}$$

Where S_{CMC} is the apparent solubility of PCE at the CMC

The measurement of PCE solubilized in aqueous surfactant solutions (at supersolubilization region obtained from the phase study since this region provides considerably high PCE solubilization, as compare to type III microemulsion, while prevent vertical migration of PCE due to the lower IFT value than type III microemulsion) were analyzed by using PerkinElmer Clarus 500 Gas Chromatography (Clarus 500, Perkin Elmer, Perkin Elmer Ltd.) with the following conditions; injector temperature at 200 ^{o}C, column of HP-5 with 30 m x 0.32 mm.ID, 0.25 µm film thickness, oven temperature at 140 – 250 ˚C, flame ionization detector at 250 ˚C, flow rate of what at 14 psi coupled with PerkinElmer Turbomatrix 40 headspace (HS) autosample (Turbomatrix 40, Perkin Elmer, Perkin Elmer Ltd.) with the following condition; thermostatting time of 30 minutes, oven temperature at 80 ˚C, needle temperature at 100 ˚C, transfer line temperature at 90 ˚C, GC cycle time of 10.0 minutes, injection time of 0.04 minutes, withdrawal time of 0.2 minutes. The following are the details of PCE measurement by GC-HS.

3.2.3.1 Standard curve determination

Calibration curve of PCE concentrations in mixed surfactant solution with a selected electrolyte concentration at the same condition obtained from phase behavior study was prepared. Three replicates of samples at the sampling size of 10 µL were injected in GC equipped with headspace autosampler at split ratio of 400:1.

3.2.3.2 Equilibrium time analysis

In order to acquire an accurate PCE solubilization in surfactant solutions, an equilibrium time of each system was investigated. This can be done by adding excess amount of PCE (1 mL) in a 7 mL of mixed surfactant solution (mixing ratio of Alfoterra:AMA = 1:1 by mole) at constant total surfactant concentration with a selected NaCl concentration in test tubes. All test tubes were sealed with caps and parafilm in order to avoid a leakage of PCE. Then, 10 µL sample from each test tube was withdrawn every 6 hours. The PCE concentration in each sample was measured by GC equipped with headspace autosampler at split ratio of 400:1. The plot between the PCE concentration and equilibrating time was made. The equilibrium time is determined as time where the PCE solubilization reaches the plateau.

3.2.3.3 Solubilization measurement

Seven mL of surfactant solutions comprised of mixed Alfoterra and AMA at the same mixing ratio of 1:1 at various total surfactant concentrations were prepared at a selected NaCl concentration in test tubes. Excess amount of PCE (1 mL) was added in the same tube where there is no headspace in the tube. The test tubes were sealed with caps and equilibrated at ambient temperature of about 28˚C for 48 hours, which is the equilibrium time obtained from the previous study. Three replicates of samples at sampling size of 10 µL at split ratio of 400:1 were analyzed for PCE solubilization in each mixed surfactant system. A plot between apparent PCE solubility versus surfactant concentration was drawn to obtain MSR as its slope and the micelle-water partitioning coefficient (K_m) parameter was then calculated.

3.2.4 Column study

The column studies were used for comparing the performance of the PCE removal by different surfactant solutions comprised of Alfoterra mixed with AMA (mixing ratio = 1:1). The column preparation was adapted from Pennel et al.(1994, 2004); Acosta et al. (2003); and Child et al. (2004).

3.2.4.1 Pore volume determination

A pore volume (PV) was first determined for a sand packed column. A glass column (2.5 cm. inner diameter, 30 cm. height) equipped with an adjustable flow adapter purchased from KONTES (model, Kontes) was packed with 20-30 mesh wet Ottawa sand under vibration in a height of 17 cm.. A pore volume of the packed column was measured by the volume of water replaced in the pore of sand packed in a column. Water was prepared in a separate container and the initial volume of water was recorded. A small amount of water was poured into the column followed by a certain amount of sand until the sand level was a little lower than that of the water. Water and sand were gradually added into the column until the desired level of sand was reached. Volume of water in the container was measured again after the column was packed. The difference of volume before and after packing indicates the pore volume since water replaces the air space in sand pore.

3.2.4.2 Sand contamination by PCE

The residue PCE saturation in the packed column was prepared for the column experiment in order to mimic the situation of PCE contamination in subsurface. Before packing, Ottawa sand was washed with water and dried in the oven at 150°C for 24 hours. The sand was then packed. Then, approximately 20 pore volumes of degassed water was pump downward into the column using a piston pump (Model QG6, Fluid Metering Inc.) at flow rate of 4 mL/min, ten times of flow rate of surfactant (Acosta et al., 2003). After that, 20 pore volumes of degassed water containing 0.01M $Ca(NO_3)_2$ was also pumped at the same flow rate in a downward direction to imitate the groundwater condition prior to contaminate the soil column with PCE (Child et al., 2004). A schematic diagram of an experimental setup for a column experiment is demonstrated in Figure 3.2.

Residual PCE saturated condition was established by injecting PCE into water-saturated sand column in up-flow mode due to PCE has greater density than water. When approximately 70% of the pore volume was occupied by PCE, free PCE phase was displaced with water in a down-flow mode in order to achieve only residue PCE in column by flushing 10 pore volumes of degassed water at a flow rate of 4 mL/min (Pennel et al., 1994). The volume of displaced free PCE was measured prior beginning the surfactant flushing. Residual saturation of PCE was calculated based on the difference of initial and final volume of the oil injecting into the column (see Appendix D). Sealed column for 1 day to allow PCE redistributed in packed sand. The volume of trapped PCE was calculated as shown in the following equation.

$$R = T - (E + F)$$

R: Volume of residual PCE in column (mL)
T: Volume of total PCE injected into column (mL)
E: Volume of PCE exited from column during PCE flooding (mL)
F: Volume of free phase PCE leaving from column during water flushing (mL)

3.2.4.3 Surfactant flushing

Selected mixed surfactant systems from the previous steps was flushed to remove residue saturated PCE in the column. Three surfactant systems of Alfoterra series mixed with AMA at mixing molar ratio = 1:1 were compared in term of PCE removal efficiency.

Mixed Alfoterra and AMA solutions with selected NaCl concentration were flushed in downward direction into column at a flow rate of 0.4 mL/min (4.77 cm/hr) to remove the trapped oil. Column effluent was collected by fraction collector (Model Frac 920, Amersham Bioscience) in every 12 mL and injected to GC equipped with headspace autosampler to determine the solubilized PCE in the flushed solution. Surfactant flushing process was terminated when the solubilized PCE in the flushed solution remain stable, less than 5% RSD.

A graph between PCE solubilization (y-axis) versus PV of surfactant solution flushed was plotted (x-axis) to compare the PCE removal efficiency among Alfoterra series. Then, the interpretation on the effects of alkyl chain length and number of PO group of Alfoterra on the PCE removal efficiency was carried out.

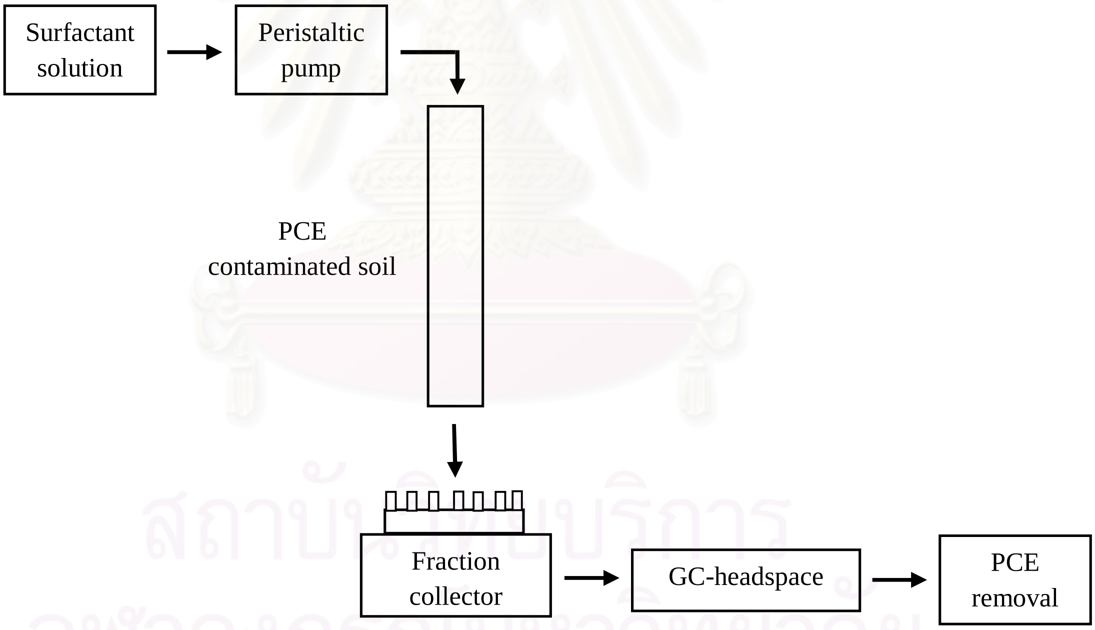

Figure 3.2: Column experiment

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Phase behavior study

Phase behavior study was the batch experiments performed to understand and examine the behavior of mixed surfactants in the presence of PCE. These experiments were used to determine the suitable salinity for creating the supersolubilization region, and to investigate the contaminant solubilization by various surfactant solutions. By decreasing the HLB of the system, the phase transition of microemulsion solution from Winsor type I to type III and to type II can be found, respectively. A decrease in HLB for a system containing anionic surfactant is usually done by raising electrolyte concentration or mixing surfactants with different HLB (Sabatini et al., 1996; and Tongcumpou et al., 2004). Nevertheless, an introduction of salt at high concentration is not a desirable method, as remediation of brine contamination is also a difficult problem (Shiau et al., 1995). Therefore, in this research, altering the HLB by a binary surfactants with different HLB was examined.

For preliminary study, the result showed that for the systems of single surfactant; Alfoterra 123-4S varying the concentration from 1 to 5 mM in the salinity scan from 0 to 5% w/w NaCl were found to be too lipophilic for PCE (HLB is too low), thus only Winsor type III microemulsion appeared. Therefore, to solve this problem, Tween 80, which has the HLB of 15 that is higher than ones of Alfoterra surfactant series, was added to be mixed with system of Alfoterra 123-4S. The NaCl was then varied from 0 to 9% w/w NaCl. The ratio of Alfoterra 123-4S mixed with Tween 80 was varied from 1:2, 1:1 and 2:1 molar ratios. The results showed that the upper layer of solution in all ratios have the precipitation of surfactant mixture before adding PCE into the solution. As a consequence, this solution was rejected for further study. Dowfax surfactant which has a very high HLB > 40 (Wu, 1996) was then introduced into the system of Alfoterra 123-4S at mixing ratio of 1:1 and 1:2 molar ratios, varying concentration of NaCl from 0 to 5% w/w. The results revealed that all solutions gave quite high IFT values of more than 1 mN/m. This would not be suitable for the further study either.

Finally, from our investigation, AMA which has HLB at 16.6 was found to be the surfactant that once mixed with Alfoterra 123-4S at mixing ratio of 1:1 and varying electrolyte concentrations from 0 to 5%w/w NaCl shows the formation of type I microemulsion at “supersolubilization” region with the appearance of the milky aqueous phase in the upper layer of solution. In addition, gel formation does not occur. Thus, the mixtures of AMA and Alfoterra series were selected for study in the next steps. Table 4.1 summarizes all preliminary results on the investigation of surfactant systems to form microemulsion with PCE and explains the reason why the system of Alfoterra mixed with AMA was selected.

Table 4.1: The results of surfactant systems investigation for PCE

System	Results
Alfoterra	Type III microemulsion occurs even without added electrolyte
Alfoterra + Tween 80	Precipitation of surfactant solution
Alfoterra + Dowfax	IFT values more than 1 mN/m
Alfoterra + AMA	Formation of Type I microemulsion with “supersolubilization” region

The preliminary study showed that the system of mixed Alfoterra and AMA was able to form microemulsion with PCE. Phase scan was carried out by varying salinity in mixed surfactant solutions and PCE in order to determine the supersolubilization region. The suitable salinity for each mixed surfactant system was selected by measuring IFT values from Spinning Drop Tensiometer incorporated with a consideration on the appearance of an aqueous phase because IFT values were not significantly different. The aqueous phase at the supersolubilization region is normally providing high solubilization of oil in water microemulsion, even though the IFT may be higher than in Type III, or middle phase microemulsion. The selected salinity of each Alfoterra mixed with AMA at mixing ratio of 1:1 in the supersolubilization region of Type I and their interfacial tension values were shown in Figured 4.1 and Table 4.2.

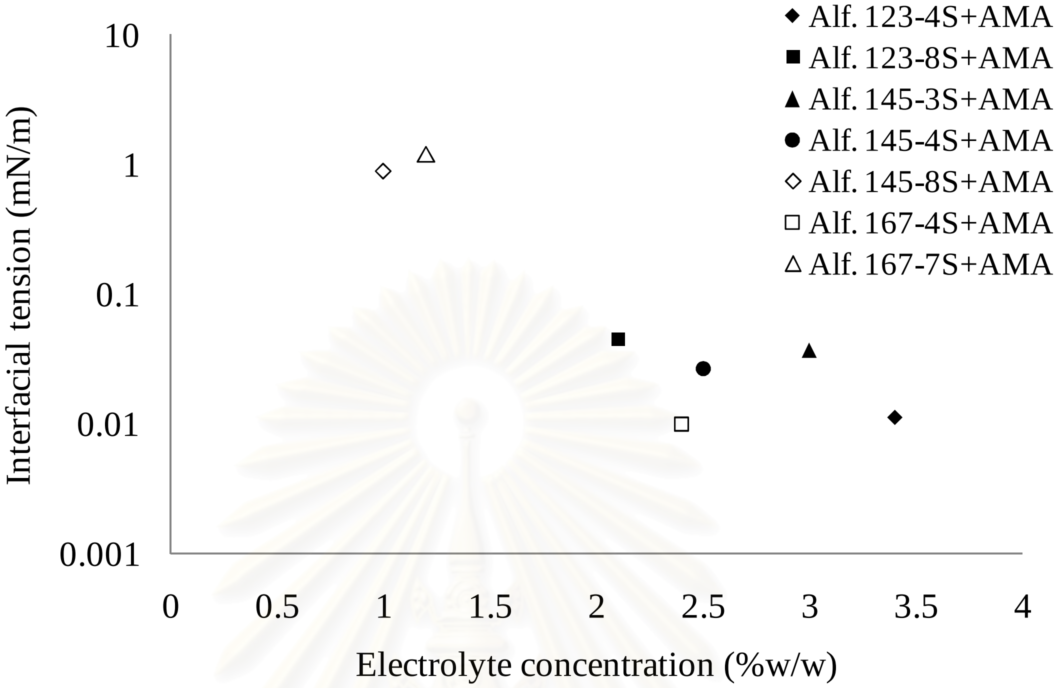

Figure 4.1: Interfacial tension (IFT) between PCE and surfactant systems (Alfoterra serie mixed with AMA) at the selected electrolyte concentrations (NaCl) in supersolubilization region of its system

According to the results shown in Figure 4.1, the IFT can be divided into 2 groups. The first group is the systems of Alfoterra 123-4S+AMA, Alfoterra 123-8S+AMA, Alfoterra 145-3S+AMA, Alfoterra 145-4S+AMA, and Alfoterra 167-4S+AMA having the IFT in the low range of 0.01 to 0.1 mN/m. The second group comprising of Alfoterra 145-8S+AMA, and Alfoterra 167-7S+AMA have their IFT values quite high at 0.875 and 1.185 mN/m, respectively. The reason for this finding was rather complicated since the chain length of surfactant tail and the number of PO group in Alfotera's structure both influent the microemulsion formation and hence, affected the interfacial curvature, which resulted to forces acting on the interface or IFT.

Table 4.2: Selected salinities at the supersolubilization for each Alfoterra serie mixed with AMA at mixing ratio = 1:1

NaCl concentration at supersolubilization (%W/W NaCl)			
	C12-13	C14-15	C16-17
3 PO	-	3.0	-
4 PO	3.4	2.5	2.4
7 PO	-	-	1.2
8 PO	2.1	1.0	-

The result in phase study showed that Alfoterra with higher degree of lipophilicity (low HLB), i.e. longer alkyl chain length and/or more PO group requires less electrolyte concentration for phase transition in order to obtain the type I “supersolubilization region”. Thus, the longer chain length and the higher the PO group result to the lower electrolyte concentration as shown in Figure 4.2 and 4.3. As a matter of fact, the longer alkyl chain length, the more hydrophobicity of the system and hence, less salt concentration is required for the supersolubilization (see Figure 4.2). For the PO which performs as an internal lipophilic linker, the result shows the same trend that the higher the PO group, the lower the electrolyte is needed for the system (see Figure 4.3). This was in agreement with previous observation that the longer alkyl chain length requires less electrolyte concentration, where C_{12-13}-$(PO)_8$-SO_4Na and C_{14-15}-$(PO)_8$-SO_4Na require electrolyte concentration of 0.21 M and 0.13 M, respectively (Witthayapanyanon et al., 2006). It is clear that when the tail length of the surfactant is smaller, the salinity needed for supersolubilization increases, suggesting from the Winsor R-ratio equation which is shown in chapter 2, the interaction $A_{SO\text{-}NET}$ is smaller. So, it requires higher electrolyte concentration to decrease $A_{SW\text{-}NET}$ in order to achieve $A_{SO\text{-}NET}$ that almost equals to $A_{SW\text{-}NET}$ (for supersolubilization where R-ratio is closed to one which occurs at the middle phase or type III microemulsion).

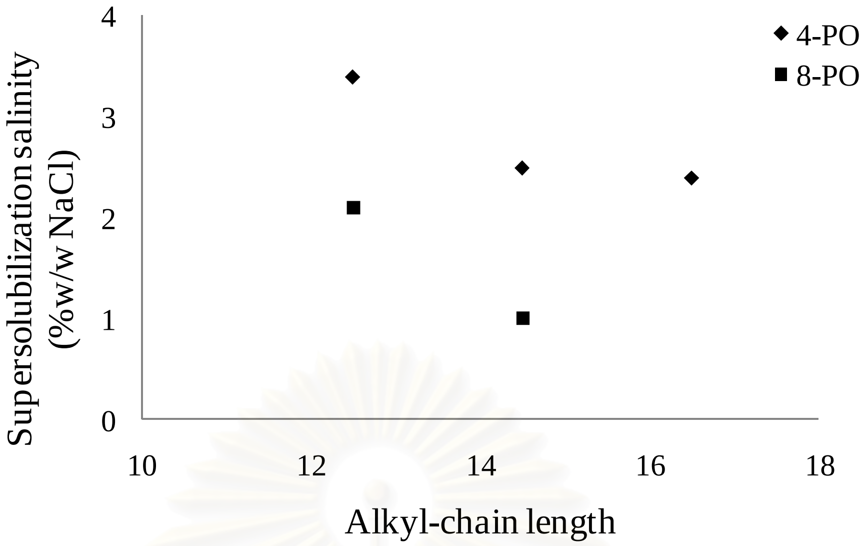

Figure 4.2: The selected salinities at the supersolubilization for the mixture of AMA and Alfoterra at different alkyl chain length (temperature = 28^{o}C)

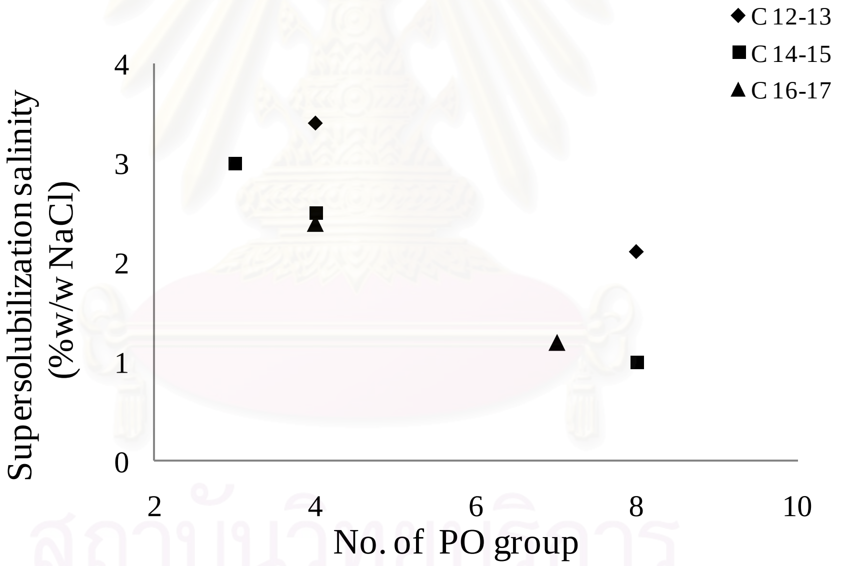

Figure 4.3: The selected salinities at the supersolubilization for the mixture of AMA and Alfoterra at different PO group (temperature = 28^{o}C)

4.2 CMC determination

For CMC study, the effect of alkyl chain length and number of PO group of Alfoterra were investigated. Figures 4.4 to 4.8, and Table 4.3 illustrate that the Alfoterra with higher lipophilicity gives the lower CMC of the system (mixture of Alfoterra and AMA), which was consistent to Witthayapanyanon et al., 2006 who found that the introduction of PO groups in Alfoterra has a significant effect on the

CMC. They also revealed that the CMC values of the extended surfactants are decreased as the alkyl chain of its tail increase, i.e. CMC of C_{12-13}-$(PO)_8$-SO_4Na and C_{14-15}-$(PO)_8$-SO_4Na at 30^{o}C are 0.130 mM and 0.033 mM, respectively. Regarding the rule of thumb that the longer alkyl chain length, the lower CMC of the surfactant, the same trend was found in this study. Suggesting that with the higher lipophilicity of Alfoterra, the less surfactant monomers are needed to form aggregate as micelle in an aqueous solution. In addition, Rosen, 2004 proposed the general rule for conventional ionic surfactant addressing that the CMC is halved by the addition of one methylene group to a straight-chain hydrocarbon of the surfactant tail. As compare to the results from this study, Alfoterra mixed with AMA, the same trend was found especially at the lower number of PO group. For 4 PO group, adding 2 methylene groups to the alkyl chain length, C 12-13 to C 14-15 and C 14-15 to C 16-17, the CMC is decreased by one-third and a quarter. However, when the number of PO group increase to 8 PO group, the data tend to deviate from the general rule. For 8 PO, adding two methylene groups from C 12-13 to C 14-15, CMC is dropped around two-third. Suggesting that the higher number of PO group caused Alfoterra, which is an extended surfactant, to be more inclined from conventional surfactant.

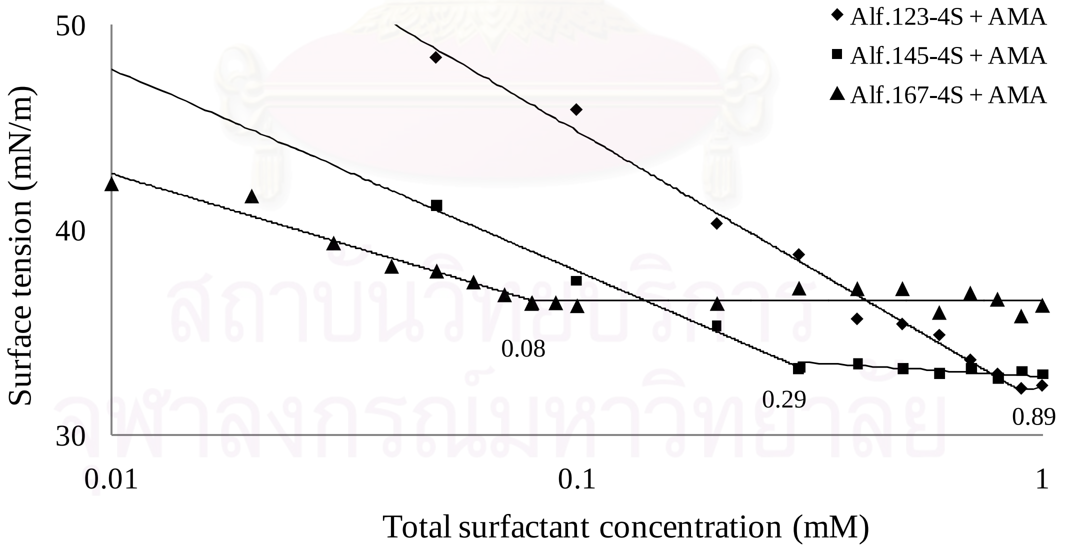

Figure 4.4: CMC of the mixture of AMA and Alfoterra 4PO (at molar ratio of 1:1) at different alkyl chain length

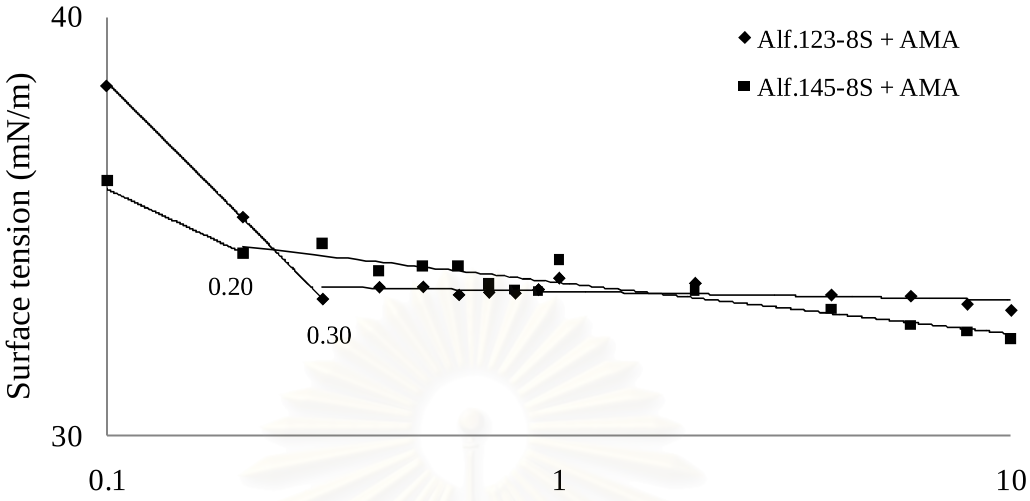

Figure 4.5: CMC of the mixture of AMA and Alfoterra 8PO (at molar ratio of 1:1) at different alkyl chain length

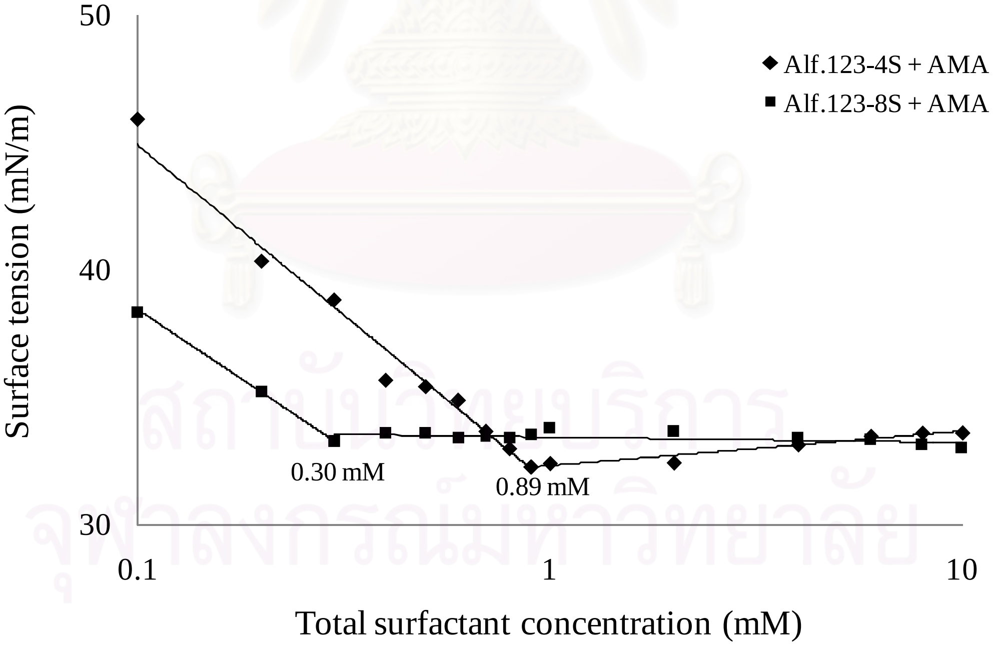

Figure 4.6: CMC of the mixture of AMA and Alfoterra C12-13 (at molar ratio of 1:1) at different number of PO group

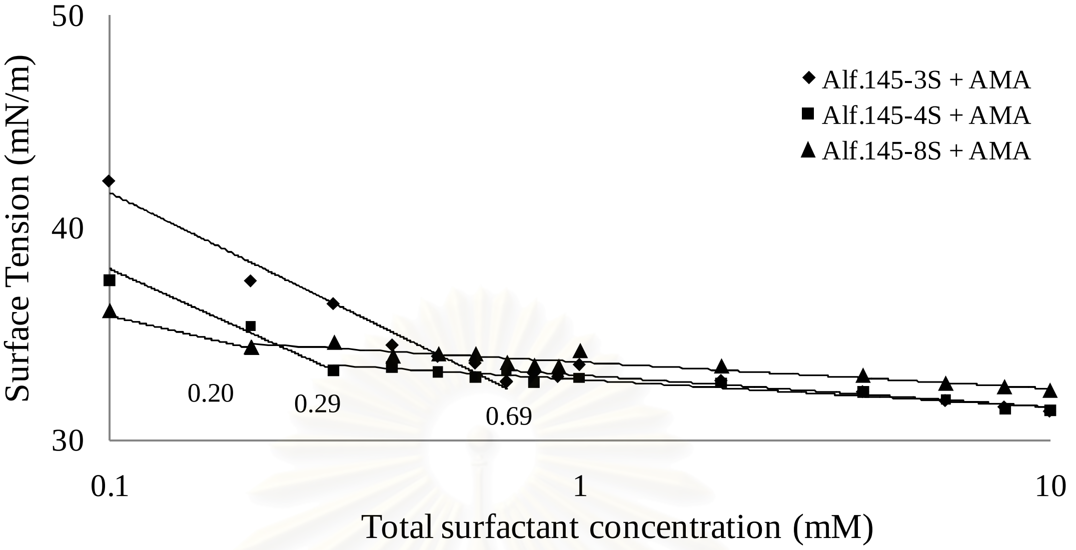

Figure 4.7: CMC of the mixture of AMA and Alfoterra C14-15 (at molar ratio of 1:1) at different number of PO group

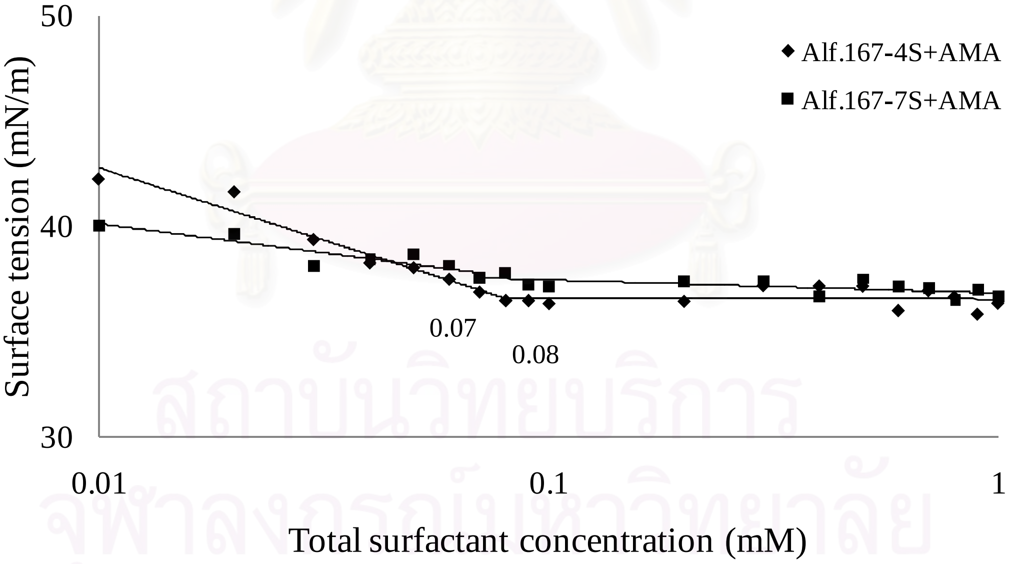

Figure 4.8: CMC of the mixture of AMA and Alfoterra C16-17 (at molar ratio of 1:1) at different number of PO group

Table 4.3: CMC of each Alfoterra serie mixed with AMA at mixing ratio = 1:1 by mole (temperature = 28°C)

Critical Micelle Concentration (mM)			
	C12-13	C14-15	C16-17
3S	-	0.69	-
4S	0.89	0.29	0.08
7S	-	-	0.07
8S	0.30	0.20	-

The conclusions of the effect of chain length and PO group in Alfoterra structure can be drawn as shown in Figures 4.9 and 4.10. It is obvious that both chain length and PO group affect on CMC in the same direction that the longer the chain length and the more the PO group, the lower CMC of the surfactant. This is due to their hydrophobic property of chain length and PO group. So, the results can be concluded that the CMC decreases with increasing degree of hydrophobicity of the surfactant. However, the effect of these two parameters seem not being linear. This may be because PO structure can exhibit both hydrophilic and hydrophobic properties as compared to chain length that is solely hydrophobic property. Consequently, for the same increase of chain length from C12-13 to C14-15 of the surfactant containing 4-PO and 8-PO group have much different in degree of CMC decreasing.

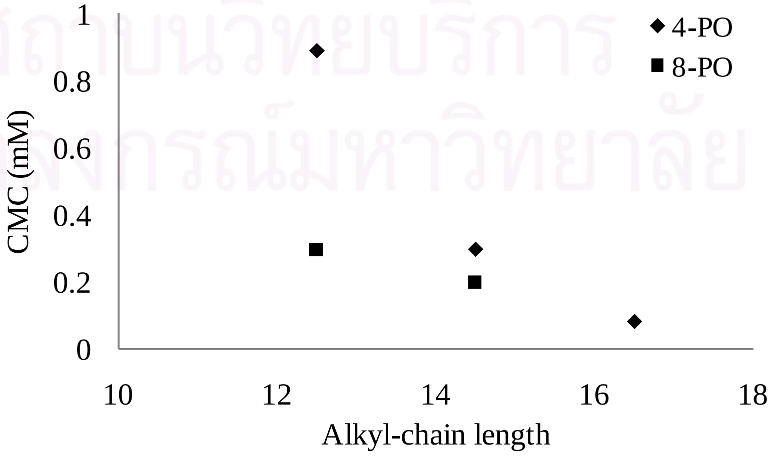

Figure 4.9: CMC of the mixture of AMA and Alfoterra at different alkyl chain length (temperature = 28°C)

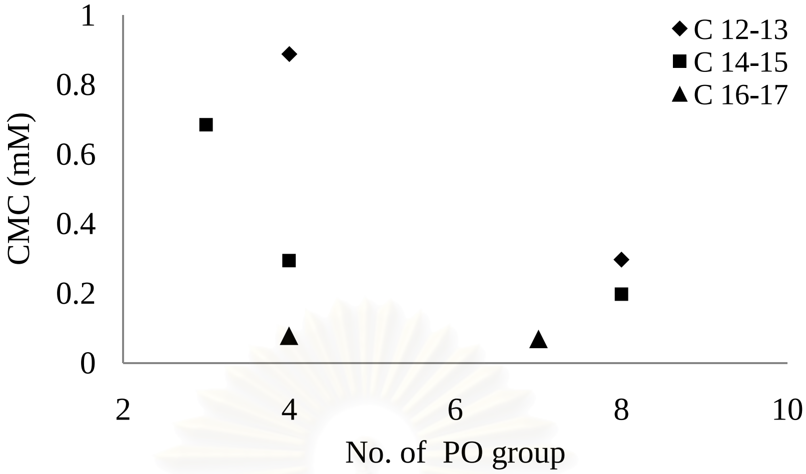

Figure 4.10: CMC of the mixture of AMA and Alfoterra at different PO group (temperature = 28°C)

This phenomenon is also true in case of constant alkyl chain length of Alfoterra but different in the number of PO as shown in Figure 4.10. At C12-13, the surfactant system is less hydrophobic, thus an increase in PO groups cause a great reduction of CMC as compared to the systems of C14-15 and C16-17, which are more hydrophobic. Especially at C16-17, the CMC remains almost constant regardless of the number of PO in the surfactant molecule.

Furthermore, the extended surfactants usually have CMC values much lower than conventional surfactant (Lange and Schwuger, 1968). Therefore, at a given concentration, extended surfactants which have lower CMC value give higher number of micelles as compared to the conventional surfactant (Shiau et al., 1994). As a consequence, PCE solubilization is greater in the surfactant solution containing lower CMC value at the same total surfactant concentration.

4.3 Solubilization study

Due to the unique molecular structure of the extended surfactant, the surfactant is stretched out further into both oil and water phases. These surfactants provide a smoother transition between the hydrophilic and lipophilic interface resulting in a more suitable environment for solubilizing hydrophilic and lipophilic molecules. It has been reported that the external lipophilic linkers orientate along the surfactant tails and promote an orientation of oil molecules into the surfactant micelles. The solubilization capacity linearly increases with increasing lipophilic linker concentration and lengthening alkyl chain length of lipophilic linker (Graciaa et al., 1993; and Uchiyama et al., 2000). However, there are some limitations of using the external linkers. Since not all linker aggregates near the interface, some partitions between the different phases (Sabatini et al., 2003). For instance, lipophilic linker molecules may solubilize in oil phase rather than partition near hydrophobic tail of surfactant. Consequently, it does not help increasing oil solubilization. In order to offset this partitioning effect, one alternative is to use the extended surfactant with internal linker. Since PO groups are considered as internal lipophilic linkers in Alfoterra molecules, we hypothesized that they can maximize PCE solubilization.

In order to examine the solubilization capacity of PCE in the system consisting of AMA mixed with Alfoterra series, the relationship between PCE solubility and total surfactant concentration was plot as shown in Appendix C. The MSR and log K_m of PCE were determined based on equation (1) and (2) shown in chapter 2, and reported in Table 4.4. The data showed that the higher alkyl chain length and the higher number of PO group give the higher MSR and log K_m values. Nevertheless, log K_m values are not significantly different. The results showed that both alkyl chain length and number of PO group in the Alfoterra structure affected the solubilization of PCE in certain degree. The data also revealed that the increasing alkyl chain length has greater effect on PCE solubilization than the increasing number of PO group. However, the effects of both factors are not linearly correlated, especially for the very long alkyl chain length i.e., C16-17, where the MSR is remarkably reduced. This may be explained by the fact that PCE is a chlorinated hydrocarbon containing chlorine atoms with polarity (log K_{ow} = 2.88, EACN = 2.9). As a consequence, to facilitate PCE in surfactant micelles, moderate chain length and appropriate number of PO group is needed to yield the maximum solubilization of PCE in the system of mixed AMA and Alfoterra surfactant. Therefore, too high or too low hydrophobicity of surfactant systems may lead to a lower solubilization capacity of surfactant for PCE.

Table 4.4: Molar solubilization ratio (MSR) and logarithm of micelle-water partitioning coefficient (Log K_m)

Alfoterra serie mix with AMA	**MSR**	**Log K_m**
$C_{12,13}H_{25,27}$-$(PO)_4$–SO_4Na	38.80	5.047
$C_{12,13}H_{25,27}$-$(PO)_8$–SO_4Na	46.70	5.048
$C_{14,15}H_{29,31}$-$(PO)_3$–SO_4Na	67.50	5.051
$C_{14,15}H_{29,31}$-$(PO)_4$–SO_4Na	106.68	5.054
$C_{14,15}H_{29,31}$-$(PO)_8$–SO_4Na	128.02	5.054
$C_{16,17}H_{33,35}$-$(PO)_4$–SO_4Na	19.42	5.034
$C_{16,17}H_{33,35}$-$(PO)_7$–SO_4Na	5.05	4.979

As compared to previous work by Shiau et al. (1994), who showed log K_m of PCE in sodium dodecyl sulfate (SDS), POE (80) sorbitan monolaurate (T-MAZ 28), POE (20) sorbitan monolaurate (T-MAZ 20), and POE (20) sorbitan monostearate (T-MAZ 60) are 4.50, 4.55, 4.90, and 4.94 respectively. They noted that log K_m of nonionic surfactant (T-MAZ surfactant) is slightly higher than that of anionic surfactant (SDS). The partitioning coefficients are similar for T-MAZ 20 and T-MAZ 60, both having 20 ethylene oxide (EO) groups. T-MAZ 28 has an intermediate partitioning coefficient as compared to the other T-MAZ surfactants and SDS. It is hypothesized that the added polarity of the T-MAZ 28 surfactant (with 80 ethylene oxide groups) is responsible for this behavior which correspond to our findings in this experiment using Alfoterra mixed with AMA that the higher hydrophilicity of surfactant, the lower PCE solubilization.

Pennel et al. (1997) reported log K_m in the range of 4.62 to 4.73 for the solubilization of PCE using a series of ethoxylated nonionic surfactants which are nonyl phenol ethoxylate (Tergitol NP-15), lauryl alcohol ethoxylate (Witconol SN-120), and polyoxyethylene (20) sorbitan monooleate (Witconol 2722) at 25°C. The results show that PCE has larger solubilization capacity in Witconol 2722 than other surfactants due to the greater alkyl chain length which also correlated with this experiment, Alfoterra mixed with AMA, that the longer the alkyl chain length, the higher the PCE solubilization.

Furthermore, Yeh et al. (2002) evaluated the PCE solubilization in solutions containing co-surfactants of ethoxylated sorbitan ester and sorbitan monooleate. They showed that the log K_m values for the solubilization of PCE for Tween 40, Tween 60, Tween 80, Tween 80+Span 80 (4:1), and Tween 80+Span 80 (1:1) are 3.89, 4.19, 4.15, 4.52, and 4.69, respectively. The explanation is that Tween 40 contains C 14 atoms leading to a lower solubility enhancement of PCE as compared to Tween 60 containing C 16 atoms which consistent with this experiment. In addition, the higher the percentage of Span 80 contained in the mixed surfactants solution, the more PCE was dissolved in the mixed surfactant solution. This trend suggests that lipophilic co-surfactant (Span 80) could significantly enhance PCE solubilization which also consistent with this experiment, Alfoterra mixed with AMA, that the higher hydrophobicity of Alfoterra, the grater solubilization of PCE.

Since PCE is quite polar, it is hypothesized not to solubilize in the core of micelle but the palisade layer. In addition, the mixed anionic-anionic surfactant may cause a loosely packing of surfactant micelle due to the repulsive forces between anionic head group. Consequently, PCE can solubilize more because of large area for PCE to solubilize.

4.4 Column study

Depending on the volume and nature of the NAPL release, the contaminant tends to be trapped in porous media at a residual saturation condition. Surfactant can significantly increase the aqueous solubility of the contaminant and thus decrease the pore volume necessary for remediation (Shiau et al., 1994).

Three surfactant solutions were chosen based on high, medium, and low value of the IFT in phase behavior study which are shown in figure 4.1, and the MSR in solubilization study which are shown in Table 4.4. Once three surfactant solutions were selected, they were applied in column study to flush sand columns at approximately 15% residual saturation of PCE in order to compare the effect of alkyl chain length and number of PO group on PCE removal. Three selected surfactant solutions were Alfoterra 123-4S+AMA (mixing ratio = 1:1 by mole), Alfoterra 145-4S+AMA (mixing ratio = 1:1 by mole), and Alfoterra 145-8S+AMA (mixing ratio =

1:1 by mole). The results of these three surfactant systems flushing in a column study were given in Figures 4.11-4.13, and the percentage of PCE removal was given in Figure 4.14. Table 4.5 provides the IFT, pore volume of surfactant flushing, PCE solubilization, PCE mobilization, trapped PCE, residual saturation, and percentage of total PCE removal for each column.

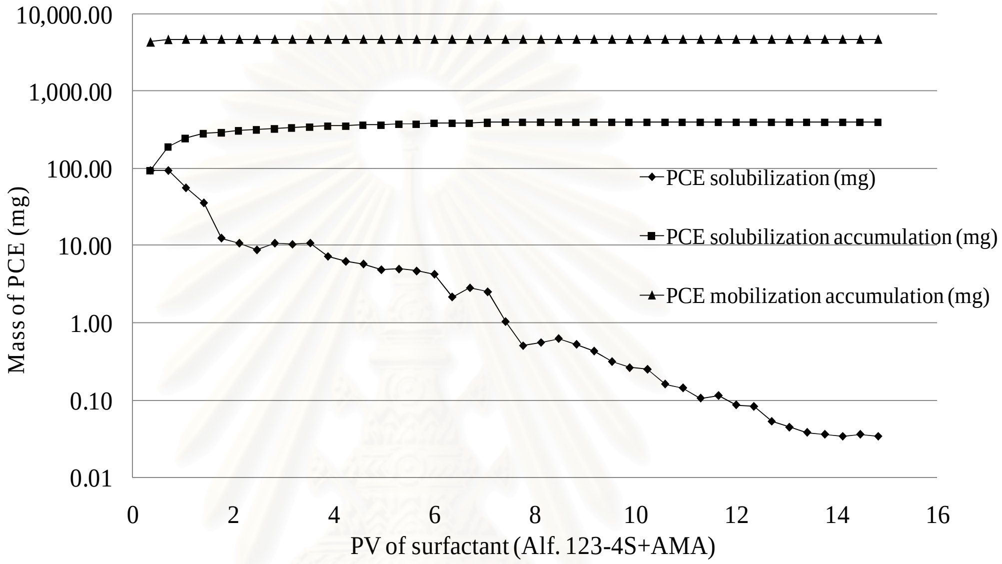

Figure 4.11: PCE removal from column using Alfoterra 123-4S+AMA (mixing ratio = 1:1) at various pore volumes

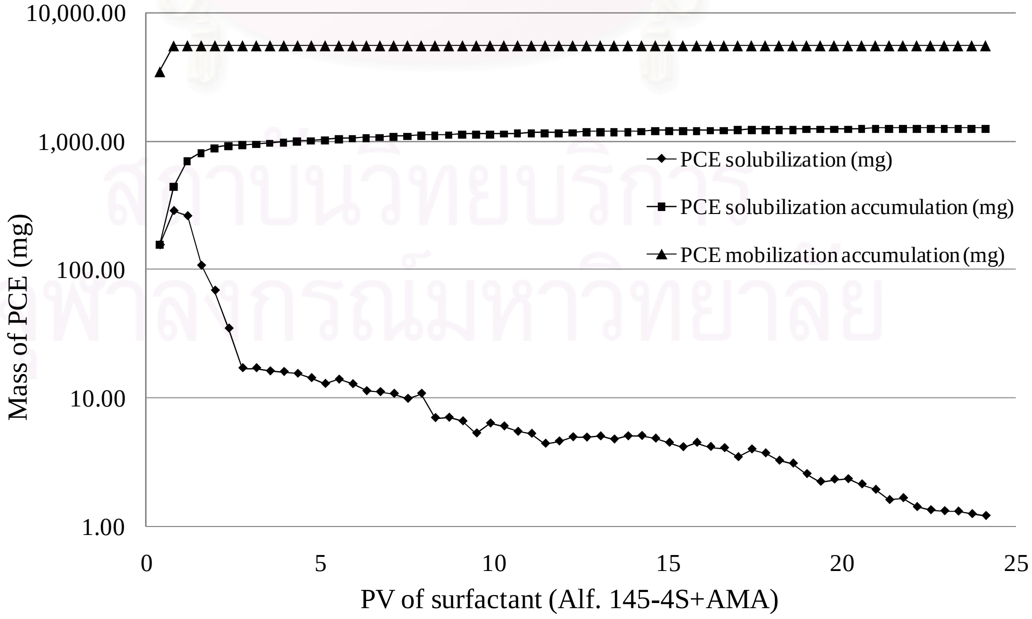

Figure 4.12: PCE removal from column using Alfoterra 145-4S+AMA (mixing ratio = 1:1) at various pore volumes

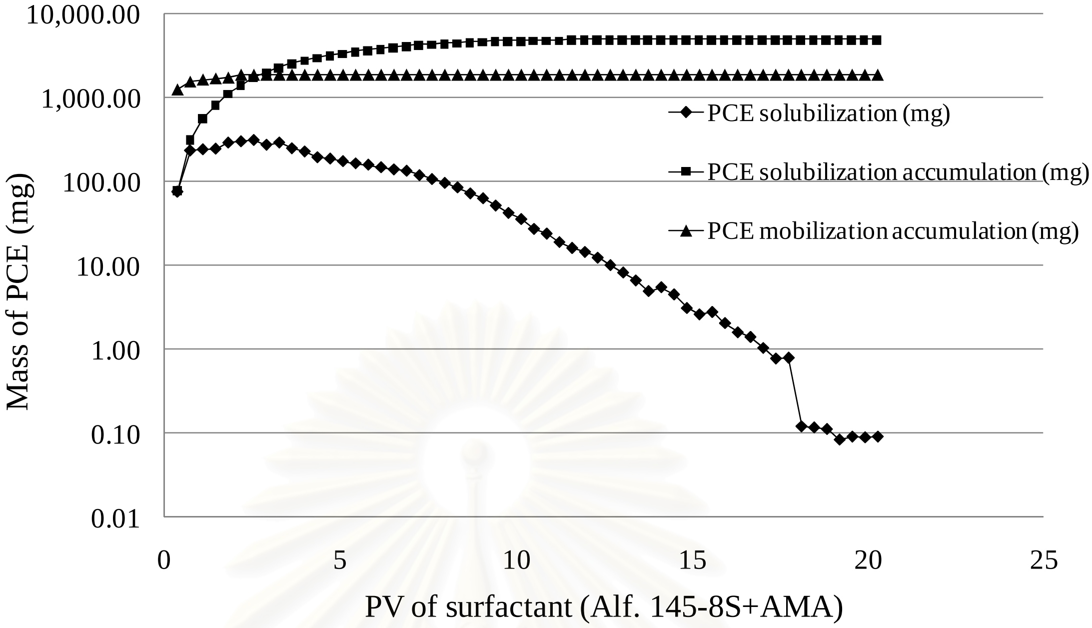

Figure 4.13: PCE removal from column using Alfoterra 145-8S+AMA (mixing ratio = 1:1) at various pore volumes

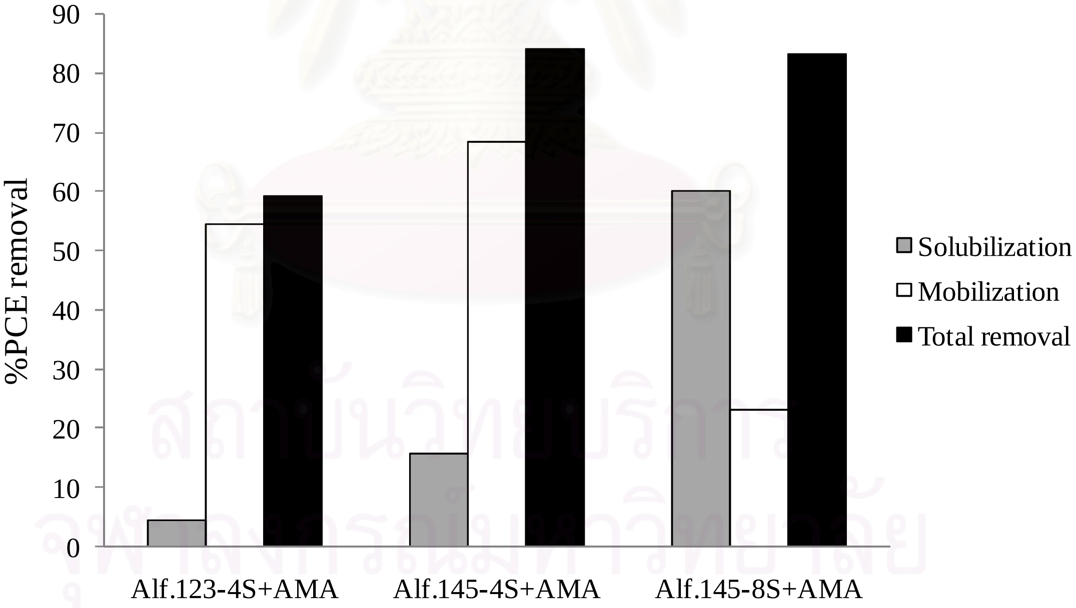

Figure 4.14: Comparison on the percentage of PCE removal using 3 surfactant systems: 1)Alfoterra 123-4S+AMA, 2)Alfoterra 145-4S+AMA, and 3)Alfoterra 145-8S+AMA

Table 4.5: Summary of all measuring parameters and results from column study at some specific pore volumes

System	IFT (mN/m)	PVs of surfactant	Solubilized accumulation (mg)	Mobilized accumulation (mg)	Trapped PCE (mg)	Residue sat.	Percentage of PCE Removal
Alf.123-4S+ AMA	0.01	15	398	4,761	8,720	15.83	59.16
Alf.145-4S+ AMA	0.03	24	1,257	5,500	8,040	15.10	84.04
Alf.145-8S+ AMA	0.87	20	4,923	1,886	8,180	15.23	83.24

The surfactant solutions used in column experiments produce PCE solubilization accumulation ranges from 398 to 4,923 mg and interfacial tensions between the surfactant solution and PCE varies from 0.01 to 0.87 mN/m. Percentages of total PCE removal are in the range of 59.16-83.24%. All three columns provide mobilization of PCE after flushing less than 1-2 PVs of surfactant (one pore volume approximately equals to 33 mL). These data suggest that the reduction in interfacial tension between PCE and surfactant aqueous phase occurred spontaneously resulting in the DNAPL mobilization at the very first few pore volumes. This finding corresponded well to one reported by Pennel et al. (1994).

The results reveal that the first surfactant system (Alfoterra 123-4S+AMA) gives the lowest PCE solubilization (4.56%) and high PCE mobilization (54.60%) same as the second surfactant system (Alfoterra 145-4S+AMA) that yields a high mobilization of 68.41%, at 15 and 24 PVs of surfactant solution, respectively. The first surfactant system gives quite low percentage of PCE removal of only 59.16%. Most of PCE removal comes from mobilization at 4,761 mg, or 54.60% while solubilization is only at 398 mg, or 4.56% of total PCE removal. Although the second surfactant system provides considerably high percentage of PCE removal (84.04%), large amount of PCE removal contributed from the mobilization of PCE (5,500 mg, or 68.41%), and only 1,257 mg, or 15.63% of total PCE removal is from solubilization. Suggesting that the interfacial tension (IFT) is responsible for trapping the oil phase, the significant reduction in IFT allows the oil to release from the porous media. Based on Figures 4.11-4.14 and Table 4.5, too low IFT i.e., for the cases of the two first system (0.01 and 0.03 mN/m) may cause very fast release of PCE and hence mobilization. However, according to Chun-Huh equation which expresses for the relationship between interfacial tension and solubilization in microemulsion system is shown as follow.

$$S = C/IFT^2$$

where S = solubilization ratio; C= constant; IFT = interfacial tension (Pope and Wade, 1995). This equation indicates that the higher the IFT, the lower the solubilization capacity of the system, which in turn means a greater number of pore volumes necessary to achieve the remediation goal. In both previous columns, the IFT surge around three times when the alkyl chain length increases from C12-13 to C14-15 caused a substantial rise in solubilization (also the same rate), 398 to 1,257 mg. It can be implied that PCE solubilization ability increasing with the longer alkyl chain length which is in agreement with the results from solubilization study.

For the third surfactant system (Alfoterra 145-8S+AMA), the percentage of total PCE removal is 83.24% within 20 PVs of surfactant. Mobilization of PCE is only at 1,886 mg (one third of Alfoterra 145-4S+AMA), or 23.06% while solubilization accounts for 4,923 mg, or 60.18% of the total PCE removal. This can be explained that mobilization is an amount of free oil that released from soil porous and not be solubilized in micelle. Thus, any surfactant system yields high solubilization, mobilization is consequentially reduced. The higher solubilization of the third system can also be explained by its number PO group. As we can observe that when number of PO group increase from 4 to 8 units, PCE solubilization increases approximately four times from 1,257 to 4,923 mg. Therefore, it can be concluded that the higher number of PO groups, the more PCE solubilization ability which is also consistent with the results from solubilization study. In addition, Alfoterra 145-8S+AMA solution does not only give a higher PCE solubilization than that of Alfoterra 145-4S+AMA, but also use less PVs of surfactant solution. As a matter of fact, it should be noted that although the mobilization was shown to be an effective means of removing residual PCE from medium, the implication of this process should be considered during the evaluation of surfactant remediation scheme especially if the contaminants are DNAPLs.

As compared to previous study by Pennel et al. (1994), two surfactant solutions containing mixtures 4% of 1:1 sodium diamyl and sodium dioctyl sulfosuccinate were used to remove PCE from Ottawa sand. The ability of a mixture was able to remove more than 99% of the residual PCE from sand columns. Mobilization of PCE was a dominant PCE removal mechanism, accounts for 82%. Since an uncontrolled mobilization of PCE is an issue of concern, IFT values should be considered. This study also indicated that the ultra-low interfacial tensions (< 0.00l mN/m) are not required to achieve significant PCE mobilization. As compare to this experiment of Alfoterra coupled with AMA, although the mixtures of 4% at 1:1 of sodium diamyl and sodium dioctyl sulfosuccinate had greater total percentage of PCE removal (99%) than Alfoterra 145-8S+AMA, large amount of PCE removal comes from mobilization which accounts for 82% while Alfoterra 145-8S+AMA has 83% of total PCE removal but around 23% of PCE is removed due to the mobilization.

In 1999, Dwarakanath et al. has studied the remediation of sand column contaminated by PCE by anionic surfactant. Surfactant composition of 2% Sodium diamyl sulfosuccinate and 2% Sodium dioctyl sulfosuccinate with $CaCl_2$ 1,300 ppm was used to remove PCE from contaminated sand which has residual saturation of PCE at 19.9%. This condition provided an IFT value at 0.01 mN/m. The result showed that mobilization was dominant, greater than 80% of PCE was removed as a free phase. These results indicated that too low IFT caused too much mobilization of PCE which consistent with this experiment using mixed surfactant of Alfoterra and AMA. As compare with Alfoterra 145-8S+AMA, the result showed lower mobilization (approximately at 20%) than 2% Sodium diamyl sulfosuccinate and 2% Sodium dioctyl sulfosuccinate due to the higher IFT value in the system of Alfoterra 145-8S+AMA.

Yeh et al. (2002), observed the flushing efficiency of PCE by two surfactant systems, only 1% Tween 80 and 1% of Tween 80 and Span 80 at mixing ratio = 4:1. The overall flushing efficiency of 1% Tween 80 was 77% with 12 PVs of flushing in silica sand. For cosurfactants of 1% Tween 80+Span 80, less flushing volumes, 7 PVs of mixed surfactants were required to achieve the same PCE removal. Suggesting that PCE can solubilize more in oilphilic Span 80 which consistent to this experiment, Alfoterra mixed with AMA, that the higher hydrophobicity, the more PCE solubilization. When compare with Alfoterra 145-8S+AMA which can remove total PCE at approximately 77% (about 20% of PCE is removed as a mobilization) in

8 PVs of surfactant lower than total volume of surfactant require for removing 77% of PCE when use only 1% Tween 80, but still higher than using 1% of Tween 80 and Span 80.

After the issue of PCE mobilization is being concerned, in 2004, Childs et al. developed gradient approach for surfactant enhanced remediation of PCE in Dover soil. Surfactant system of 5% Dowfax, 3% AMA with slowly increased NaCl and $CaCl_2$ concentrations, was used in their study. Two steps of electrolyte were implemented, they revealed that the flushing with only $CaCl_2$ yielded 6.3 mN/m of IFT value, and with 3% NaCl yielded 1 mN/m of IFT value. However, they allowed a more gradual transition between these two IFT values by flushing other two different electrolytes; 3% NaCl and 3% $CaCl_2$ which providing 0.5 mN/m, and 3% NaCl mixed with 6% $CaCl_2$ which providing 0.3 mN/m. They observed that only 6% of PCE was removed as mobilization. As compare with our system in this study; Alfoterra 145-8S+AMA, the system of 5% Dowfax + 3% AMA with gradually increased NaCl and $CaCl_2$ concentrations was almost completely solve the problem of PCE mobilization, which is far better than using Alfoterra 145-8S+AMA with constant 1% NaCl. Only one point which should be noted here is that the system of Alfoterra 145-8S+AMA with constant 1% NaCl uses less concentrations for electrolyte and total concentration than the system of 5% Dowfax+3% AMA with gradient electrolyte approach.

Therefore, from the previous results, it can be concluded that not only the initial IFT should be low enough to generate oil release from soil porous, but that the gradient steps must also be applied in order to enhance solubilization and hence prevent PCE mobilization.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study introduced the extended anionic surfactants, Alfoterra, to enhance the PCE removal from sand. The specific objectives are to study the solubilization of PCE in microemulsion system formed by seven types of extended surfactants, and to investigate the effects of alkyl chain length and number of PO groups in Alfoterra molecule on the PCE removal.

In the phase behavior study, the salinity at supersolubilization for each Alfoterra mixed with AMA system was firstly determined by measuring the IFT incorporated and considering the appearance of an aqueous phase. The result showed that Alfoterra with more lipophilicity required less electrolyte concentration for decreasing HLB of the system to form the Winsor type I microemulsion at the supersolubilization region.

For the CMC study, the data illustrated that the Alfoterra with the higher lipophilicity (longer carbon chain length or more PO groups) showed the lower CMC. However, at high number of PO group i.e. 8 PO group, the CMC reduction tend to deviate from general rule for conventional ionic surfactant which address that that the CMC is halved by the addition of one methylene group to a straight-chain hydrocarbon of the surfactant tail.

Based on the solubilization study, the results showed that both alkyl chain length and number of PO group in the structure of Alfoterra affected the solubilization of PCE. It can be concluded that the longer the alkyl chain length and the higher the number of PO group give the higher MSR and log K_m values. The results also illustrated that the increasing alkyl chain length has greater effect on PCE solubilization than the increasing number of PO group. The best system providing the greatest PCE solubilization was Alfoterra 145-8S+AMA. However, the effects of both factors are not linearly correlated, especially for the very long alkyl chain length i.e., C16-17, where the MSR is remarkably reduced. Since PCE is a hydrophobic oil but exhibit polarity from containing chlorine in its structure, PCE is more favorable to be solubilized into the surfactant micelles with moderate chain length and appropriate number of PO group. Ultimately, in the column study, three surfactant solutions: Alfoterra 123-4S+AMA, Alfoterra 145-4S+AMA, and Alfoterra 145-8S+AMA were selected to be used to compare the effect of alky chain length and number of PO group on PCE removal from sand packed in column with residual saturation of PCE. The results showed that the longer the alkyl chain length and the higher the number of PO group yielded the greater percentage of PCE removal. Total PCE can be removed from contaminated sand in a range of 59-84% using 3 surfactant solutions mentioned above. The solubilization accumulation of PCE varies from 398-4,923 mg, or 4.56-60.18% of total PCE removal, while the mobilization of PCE as a free oil phase accounts for 1,886-5,500 mg, or 23.06-68.41% of total PCE removal. Alfoterra 145-8S+AMA, performs the best system for PCE removal, gives the highest PCE solubilization (60%), and lowest PCE mobilization (23%). In addition, all three columns showed the mobilization of PCE after flushing at about 1-2 PVs of surfactant due to a great reduction in IFT between the trapped PCE and surfactant solution.

5.2 Recommendation

This experiment tried to create the type I microemulsion at “supersolubilization” region instead of type III microemulsion in order to avoid the vertical migration of PCE that is recognized to be occurred at too low IFT. However, there was still large amount of PCE removed by a contribution of mobilization (23%) even though in the best system, Alfoterra 145-8S+AMA, was used in column study. Another point to concern is the evaporation of PCE because some PCE may loss while experimenting the column study. In this experiment, only PCE in effluent is considered. So, if PCE evaporation is concerned, PCE removal efficiency will be higher than in this experiment. In order to solve PCE evaporation problem, mass balance should be done. And, the results would be accepted when %RSD less than 10%.

Although mobilization was shown to be an effective means of removing residual PCE from Ottawa sand, the implication of these surfactant systems should be considered upon an evaluation of surfactant remediation scheme owing to a vertical migration problem of this DNAPL contaminant. Therefore, the gradient approach using these three surfactant systems should be investigated in the future study. As a matter of fact, type III microemulsion, which has the lowest IFT in the Winsor diagram, can mobilize and elute more PCE than the solubilization process (Shiau et al., 1995). Then, the type III microemulsion should be used coupled with the gradient approach by trying not to get too low IFT at the very first step but gradually decrease it in order to prevent the mobilization of PCE. Thus, the electrolyte concentration should be slightly ramped up and the IFT would gradually drop as a result (Child et al., 2004).

Ultimately, the disadvantage of extended surfactants is that they tend to form gel phase at high surfactant concentration since theirs molecule are large. Because gel may cause pore plugging while implementing SEAR in the sites. However, the surfactant formulation with hydrophilic linkers can overcome this tendency to form gels. Thus, when using extended surfactants, a combination of extended surfactants and linker may enhance the effectiveness of the system (Sabatini et al., 2003).

5.3 Management

There are many conventional technologies for PCE removal which are:

- Excavation processes: hauling the contaminated soil to a regulated landfill, but can also involve aerating the excavated material in the case of volatile organic compounds.

- Bioremediation: used in conjunction with a pump and treat system. In bioremediation, either naturally occurring or specially bacteria are used to consume contaminants from extracted groundwater. Many times the groundwater is recycled to allow for continuously flowing water and enhanced bacteria population growth. However, care must be taken to ensure that a sharp change in the groundwater chemistry does not kill the bacteria (such as a sudden change in pH).

- Pump and treat: involves pumping out contaminated groundwater with the use of a vacuum pump, and allowing the extracted groundwater to be purified by chemical reagents such as flocculants and sand filters to decrease the contamination of groundwater. Air stripping is a method that can be effective for volatile pollutants. Pump and treat may be a good method to quickly reduce high concentrations of pollutants. But, it is more difficult to reach sufficiently low concentrations to satisfy remediation standards, due to the equilibrium of absorption/desorption processes in the soil.

- In situ oxidation technologies: have become popular for remediation of a wide range of soil and groundwater contaminants. Remediation by chemical oxidation involves the injection of strong oxidants such as hydrogen peroxide, ozone gas, potassium permanganate. Oxygen gas or ambient air can also be injected as a more mild approach. The disadvantage of this approach is the possibility of less contaminant destruction by natural attenuation if the bacteria which normally live in the soil prefer a reducing environment. The degradation of PCE can be occurred within 65 days. The by-products are TCE, cis-dichloroethylene, vinyl chloride, ethylene, and ethane. In addition, the injection of gases into the groundwater may also cause contamination to spread faster than normal depending on the site's hydrogeology.
- Soil vapor extraction (SVE) is an effective remediation technology for soil. "Multi Phase Extraction" (MPE) is also an effective remediation technology when soil and groundwater are to be remediated coincidentally. SVE and MPE utilize different technologies to treat the off-gas volatile organic compounds (VOCs) generated after vacuum removal of air and vapors (and VOCs) from the subsurface and include granular activated carbon (most commonly used historically), thermal and/or catalytic oxidation and vapor condensation. Generally, carbon is used for low (<500ppm) VOC concentration vapor streams, oxidation is used for moderate (up to 4,000 ppm) VOC concentration streams, and vapor condensation is used for high (>4,000 ppm) VOC concentration vapor streams.
- Surfactant Enhanced Aquifer Remediation process: involves the injection of surfactants into the subsurface to enhance desorption a non aqueous phase liquid (NAPL). This approach provides a cost effective (www.wikipedia.com) and permanent solution to sites that have been previously unsuccessful utilizing other remedial approaches. This technology is also successful when utilized as the initial step in a multi faceted remedial approach utilizing SEAR, then in situ oxidation, bioremediation enhancement or soil vapor extraction (SVE).

For the extended surfactants which are used in this experiment usually have CMC values much lower than conventional surfactant (Lange and Schwuger, 1968). Therefore, at a given concentration, extended surfactants which have lower CMC value give higher number of micelles as compared to the conventional surfactant (Shiau et al., 1994). As a consequence, PCE solubilization is greater in the surfactant solution containing lower CMC values at the same total surfactant concentration bring on a higher efficiency. Furthermore, using of extended surfactants instead of conventional surfactants require lower cost due to less surfactant concentration is needed.

However, for Alfoterra 145-8S+AMA which shows the largest PCE solubilization removal in this column experiment, when it is implemented in the sites, the efficiency will be lower than in this experiment. Since in the real soil (not like Ottawa sand which is used in this experiment) has organic content and charge of soil media itself, some surfactant may loss due to the adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter ions in soil media. In addition, PCE sorption with the organic content in soil will cause PCE to be removed more difficult because of a stronger interaction between two organic contents. The schematic diagram of surfactant enhanced aquifer remediation management is shown in Figure 5.1 (Childs et al., 2006).

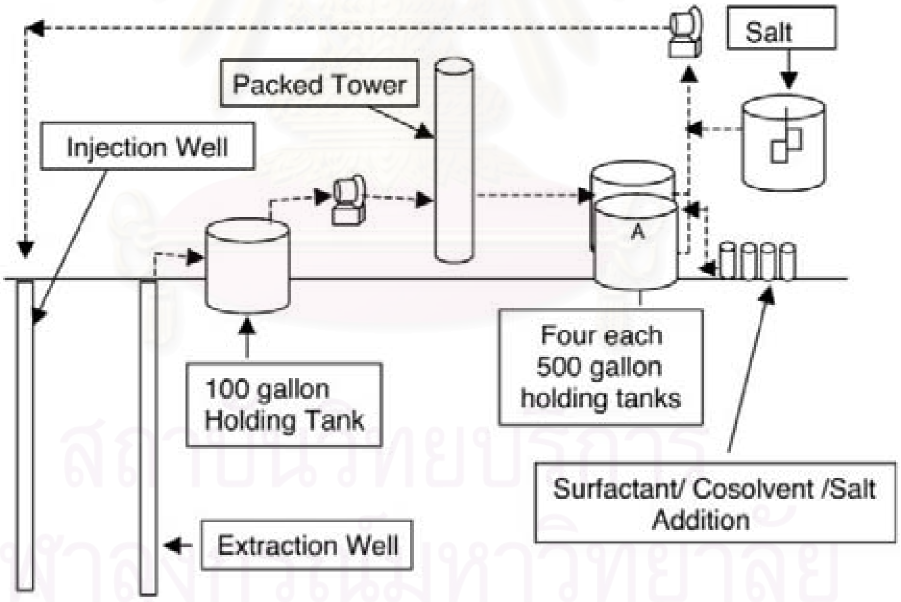

Figure 5.1: Schematic diagram of SEAR technology. Adapted from Childs et al., 2006.

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APPENDICES

Appendix A: Experimental Data of Phase Behavior Study

Table A-1 Interfacial Tension of Alfoterra 123-4S and AMA at mixing ratio = 1:1

Vial	Interfacial Tension (mN/m)			Average IFT
0.0% NaCl	4.4991	4.5593	5.5452	4.8679
1.0% NaCl	0.9446	0.8098	0.8469	0.8671
2.0% NaCl	0.3916	0.4765	0.4089	0.4257
3.0% NaCl	0.0563	0.0649	0.0647	0.0620
3.1% NaCl	0.0227	0.0229	0.0231	0.0229
3.2% NaCl	0.0214	0.0246	0.0192	0.0217
3.3% NaCl	0.0143	0.0130	0.0150	0.0141
3.4% NaCl	0.0118	0.0107	0.0107	0.0111
3.5% NaCl	0.0295	0.0271	0.0257	0.0274
3.6% NaCl	N/A			N/A
3.7% NaCl	N/A			N/A
3.8% NaCl	0.0386	0.0438		0.0412
3.9% NaCl	0.0312	0.0347	0.0364	0.0341
4.0% NaCl	0.0234	N/A	N/A	0.0234
4.2% NaCl	0.0494	0.0476	0.0374	0.0448
4.4% NaCl	0.0399	0.0397	0.0461	0.0419
4.6% NaCl	0.0703	0.0672	0.0641	0.0672
4.8% NaCl	0.1034	0.1422	N/A	0.1228
5.0% NaCl	0.1093	0.1009	0.1093	0.1065

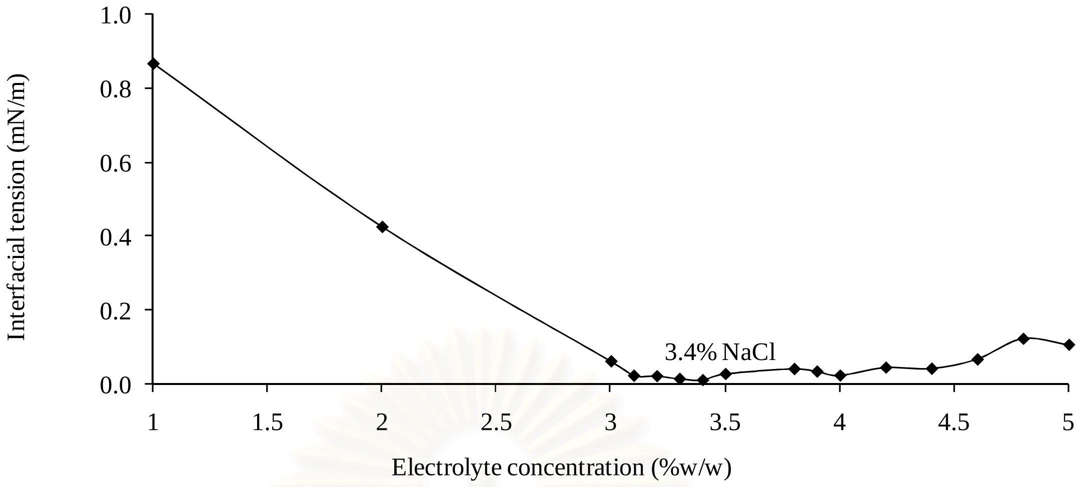

Figure A-1: Interfacial tension of Alfoterra 123-4S mixed with AMA (mixing ratio = 1:1)

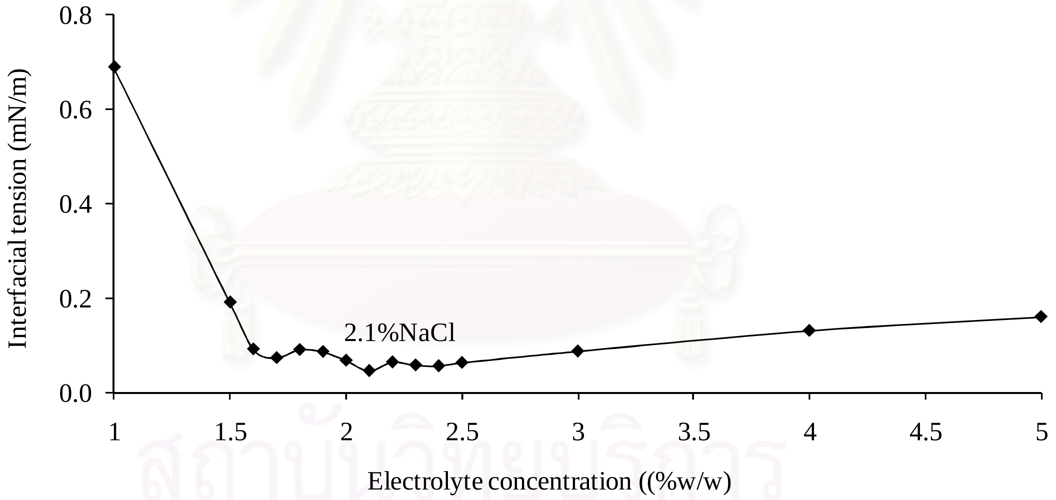

Figure A-2: Interfacial tension of Alfoterra 123-8S mixed with AMA (mixing ratio = 1:1)

Table A-2 Interfacial Tension of Alfoterra 123-8S and AMA at mixing ratio = 1:1

Vial	Interfacial Tension (mN/m)			Average IFT
0.0% NaCl	0.7579	0.7458	0.7127	0.7388
1.0% NaCl	0.7106	0.7241	0.6270	0.6872
1.5% NaCl	0.1399	0.2685	0.1599	0.1894
1.6% NaCl	0.0947	0.0868	0.0891	0.0902
1.7% NaCl	0.0722	0.0746	0.0685	0.0718
1.8% NaCl	0.0858	0.0886	0.0923	0.0889
1.9% NaCl	0.0712	0.0915	0.0914	0.0847
2.0% NaCl	0.0664	N/A	N/A	0.0664
2.1% NaCl	0.0459	0.0426	0.0448	0.0444
2.2% NaCl	0.0699	0.0583	0.0594	0.0625
2.3% NaCl	0.0616	0.0536	0.0535	0.0562
2.4% NaCl	0.0541	0.0525	0.0567	0.0544
2.5% NaCl	0.0643	0.0611	0.0591	0.0615
3.0% NaCl	0.0854	0.0843	0.0877	0.0858
4.0% NaCl	0.1219	0.1290	0.1372	0.1294
5.0% NaCl	0.1589	0.1620	0.1551	0.1587

Table A-3 Interfacial Tension of Alfoterra 145-3S and AMA at mixing ratio = 1:1

Vial	Interfacial Tension (mN/m)			Average IFT
0.0% NaCl	0.7939	0.7552	0.7202	0.7564
0.5% NaCl	0.6387	0.6431	0.6430	0.6416
1.0% NaCl	0.4523	0.4452	0.4229	0.4401
1.5% NaCl	0.1916	0.2126	0.1913	0.1985
2.0% NaCl	0.0541	0.0482	0.0486	0.0503
2.5% NaCl	0.0489	0.0474	0.0390	0.0451
2.9% NaCl	0.0513	0.0448	0.0453	0.0471
3.0% NaCl	0.0321	0.0408	0.0366	0.0365
3.1% NaCl	0.0374	0.0308	0.0282	0.0322
3.3% NaCl	0.0269	0.0326	0.0298	0.0298
3.5% NaCl	0.0260	0.0273	0.0287	0.0273
3.7% NaCl	0.0358	0.0296	0.0349	0.0334
3.9% NaCl	0.0481	0.0442	0.0395	0.0439
4.0% NaCl	0.0562	0.0428	N/A	0.0495
4.5% NaCl	0.0733	0.0761	0.0752	0.0748
5.0% NaCl	0.1061	0.1042	0.1039	0.1047

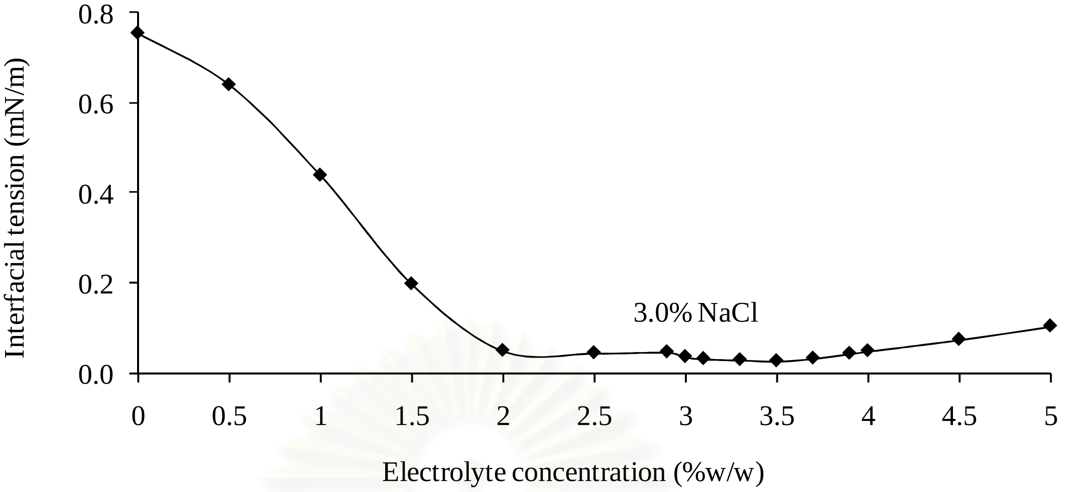

Figure A-3: Interfacial tension of Alfoterra 145-3S mixed with AMA (mixing ratio = 1:1)

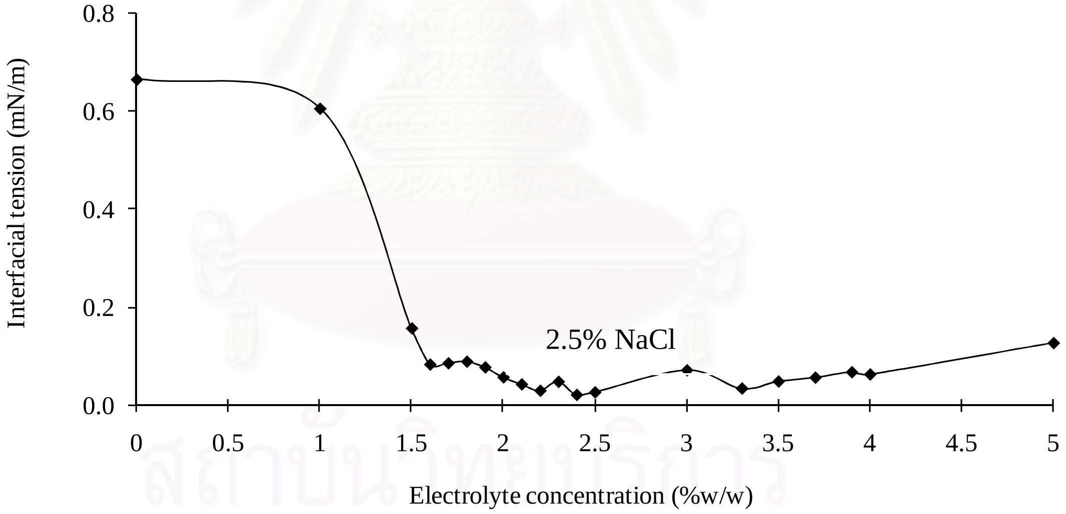

Figure A-4: Interfacial tension of Alfoterra 145-4S mixed with AMA (mixing ratio = 1:1)

Table A-4 Interfacial Tension of Alfoterra 145-4S and AMA at mixing ratio = 1:1

Vial	Interfacial Tension (mN/m)			Average IFT
0.0% NaCl	0.6790	0.6535	0.6609	0.6645
1.0% NaCl	0.6381	0.6028	0.5747	0.6052
1.5% NaCl	0.1872	0.1494	0.1336	0.1567
1.6% NaCl	0.0827	0.0812	0.0848	0.0829
1.7% NaCl	0.0848	0.0839	0.0875	0.0854
1.8% NaCl	0.0858	0.0914	0.0884	0.0885
1.9% NaCl	0.0702	0.0783	0.0817	0.0767
2.0% NaCl	0.0576	0.0554	0.0560	0.0564
2.1% NaCl	0.0450	0.0489	0.0335	0.0425
2.2% NaCl	0.0254	0.0370	0.0245	0.0289
2.3% NaCl	0.0447	0.0456	0.0522	0.0475
2.4% NaCl	0.0199	0.0197	0.0216	0.0204
2.5% NaCl	0.0249	0.0263	0.0268	0.0260
2.7% NaCl	N/A			N/A
2.9% NaCl	N/A			N/A
3.0% NaCl	0.0656	0.0766		0.0711
3.1% NaCl	N/A			N/A
3.3% NaCl	0.0327	0.0335	0.0341	0.0334
3.5% NaCl	0.0122	0.0119	0.1200	0.0480
3.7% NaCl	0.0582	0.0545	0.0546	0.0558
3.9% NaCl	0.0623	0.0719	0.0676	0.0673
4.0% NaCl	0.0638	0.0597	0.0638	0.0624
5.0% NaCl	0.1144	0.1218	0.1437	0.1266

Table A-5 Interfacial Tension of Alfoterra 145-8S and AMA at mixing ratio = 1:1

Vial	Interfacial Tension (mN/m)			Average IFT
0.0% NaCl	1.4275	1.4573	1.5319	1.4722
0.5% NaCl	1.1073	1.1143	1.3866	1.2027
0.6% NaCl	1.1609	1.1495	1.1645	1.1583
0.7% NaCl	1.1155	1.1059	1.1078	1.1097
0.8% NaCl	1.0716	1.0027	1.0776	1.0506
0.9% NaCl	1.0154	0.9699	0.9155	0.9669
1.0% NaCl	0.8970	0.8633	0.8633	0.8746
1.1% NaCl	0.8312	0.7518	0.7424	0.7751
1.2% NaCl	0.7121	0.7836	0.7256	0.7404
1.3% NaCl	0.7591	0.7350	0.7033	0.7325
1.4% NaCl	0.6704	0.7066	0.6593	0.6788
1.5% NaCl	0.5429	0.5330	0.5087	0.5282
1.6% NaCl	0.1328	0.1935	0.1375	0.1546
1.7% NaCl	0.1344	0.1321	0.1511	0.1392
1.8% NaCl	0.0830	0.0863	0.0934	0.0876
1.9% NaCl	0.0732	0.0799	0.0778	0.0770
2.0% NaCl	0.0599	0.0465	0.0666	0.0577
2.1% NaCl	0.0401	0.0402	0.0548	0.0450
2.2% NaCl	0.0362	0.0386	0.0322	0.0357
2.3% NaCl	0.0201	0.0215	0.0325	0.0247
2.4% NaCl	0.0464	0.0568	0.0302	0.0445
2.5% NaCl	0.0585	0.0558	0.0638	0.0594

Vial	Interfacial Tension (mN/m)			Average IFT
2.6% NaCl	0.0587	0.0660	0.0996	0.0951
2.7% NaCl	0.0994	0.0862	0.0803	0.0683
2.8% NaCl	0.1045	0.1102	0.0996	0.0951
2.9% NaCl	0.0758	0.0784	0.1045	0.1064
3.0% NaCl	0.1379	0.1263	0.0723	0.0755
4.0% NaCl	0.1448	0.1691	0.1219	0.1287
5.0% NaCl	0.1989	0.1909	0.1730	0.1623

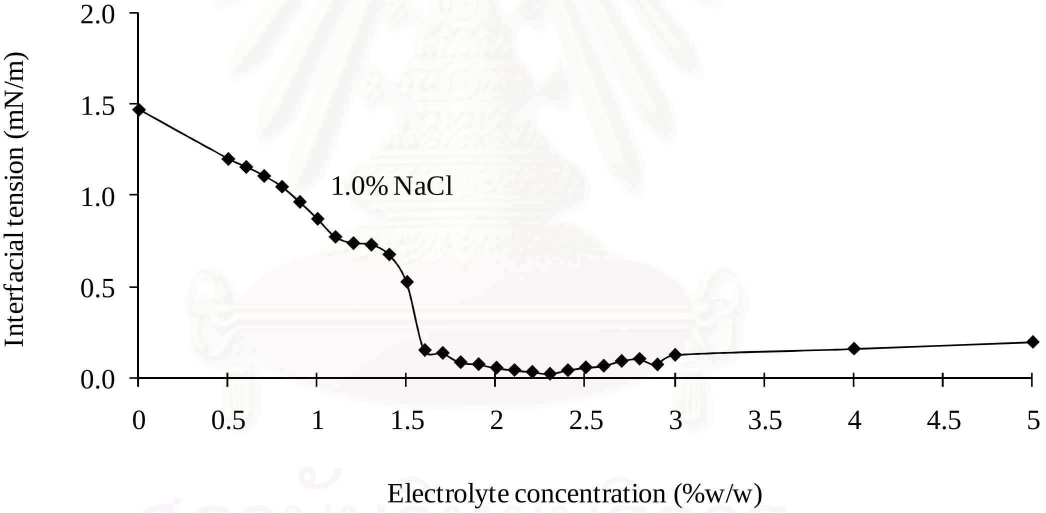

Figure A-5: Interfacial tension of Alfoterra 145-8S mixed with AMA (mixing ratio = 1:1

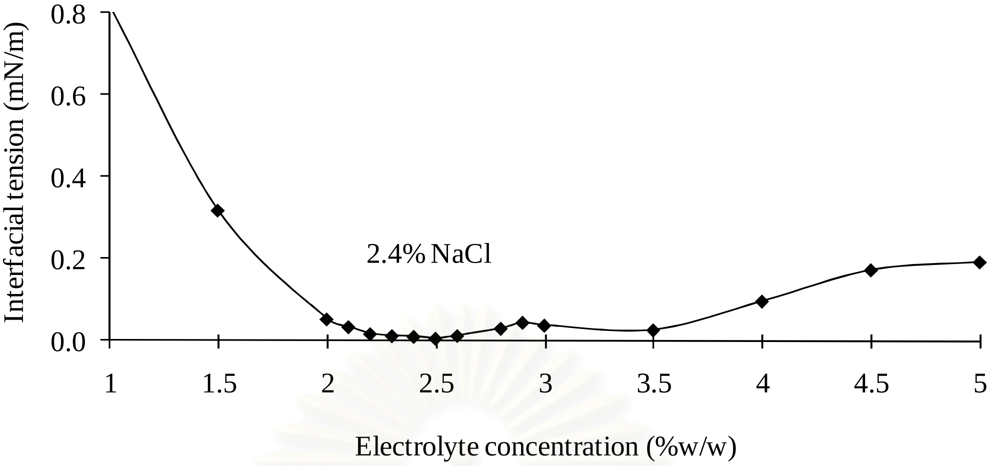

Figure A-6: Interfacial tension of Alfoterra 167-4S mixed with AMA (mixing ratio = 1:1)

Table A-6 Interfacial Tension of Alfoterra 167-4S and AMA at mixing ratio = 1:1

Vial	Interfacial Tension (mN/m)			Average IFT
0.0% NaCl	0.8852	0.8344	0.7867	0.8354
0.5% NaCl	0.5552	0.5448	0.7710	0.6237
1.0% NaCl	0.8674	0.8246	0.7710	0.8210
1.5% NaCl	0.3169	0.2793	0.3569	0.3177
2.0% NaCl	0.0542	0.0536	0.0503	0.0527
2.1% NaCl	0.0331	0.0325	0.0348	0.0335
2.2% NaCl	0.0162	0.0170	0.0169	0.0167
2.3% NaCl	0.0117	0.0119	0.0115	0.0117
2.4% NaCl	0.0104	0.0097	0.0098	0.0099
2.5% NaCl	0.0054	0.0054	0.0052	0.0053
2.6% NaCl	0.0129	0.0115	0.0117	0.0120
2.7% NaCl	N/A			N/A
2.8% NaCl	0.0255	0.0321	0.0315	0.0297
2.9% NaCl	0.0411	0.0447	0.0467	0.0442
3.0% NaCl	0.0350	0.0395	0.0370	0.0372
3.5% NaCl	0.0255	0.0268	0.0248	0.0257
4.0% NaCl	0.0981	0.1067	0.0832	0.0960
4.5% NaCl	0.1528	0.1649	0.1987	0.1722
5.0% NaCl	0.1913	0.1531	0.2301	0.1915

Table A-7 Interfacial Tension of Alfoterra 167-7S and AMA at mixing ratio = 1:1

Vial	Interfacial Tension (mN/m)			Average IFT
0.0% NaCl	1.3346	1.7081	1.8319	1.6249
0.5% NaCl	1.5544	1.6736	1.6006	1.6095
1.0% NaCl	0.8864	0.9035	0.9082	0.8993
1.1% NaCl	1.7938	1.7945	1.8599	1.8161
1.2% NaCl	1.2037	1.1945	1.1565	1.1849
1.3% NaCl	1.0503	0.9436	0.9418	0.9786
1.4% NaCl	0.9783	0.9926	1.0170	0.9960
1.5% NaCl	0.3736	0.2816	0.3322	0.3291
1.6% NaCl	0.1336	0.1378	0.1341	0.1352
1.7% NaCl	0.1229	0.1232	0.1218	0.1226
1.8% NaCl	0.1220	0.1195	0.1219	0.1211
2.0% NaCl	0.1254	0.1288	0.1296	0.1279
2.5% NaCl	0.0781	0.0552	0.1012	0.0781
3.0% NaCl	0.1027	0.1032	0.1084	0.1048
3.5% NaCl	0.1167	0.1215	0.1305	0.1229
4.0% NaCl	0.1489	0.1529	0.1444	0.1487
4.5% NaCl	0.1392	0.1654	0.1842	0.1629
5.0% NaCl	0.1946	0.2000	0.2503	0.2150

N/A : indicates value cannot measured

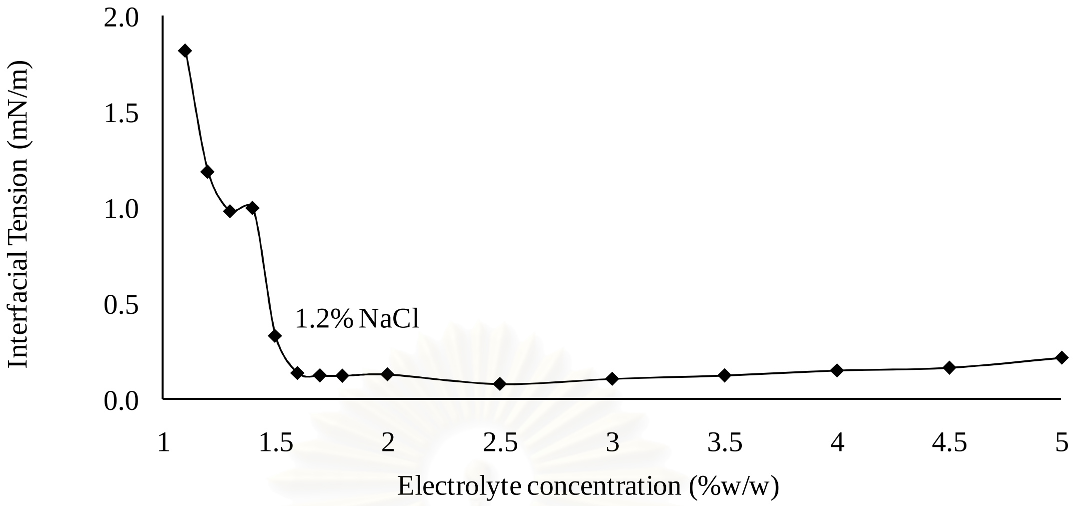

Figure A-7: Interfacial tension of Alfoterra 167-7S mixed with AMA (mixing ratio = 1:1)

Appendix B: Experimental Data of Critical Micelle Concentration Study

Table B-1: Surface tension of Alfoterra 123-4S+AMA

Total Concentration (mM)	Surface tension 1	Surface tension 2	Average Surface Tension
0.05	48.48	48.47	48.48
0.10	46.04	45.80	45.92
0.20	40.06	40.64	40.35
0.30	38.55	39.12	38.84
0.39	35.98	35.39	35.69
0.49	35.10	35.77	35.44
0.59	35.05	34.75	34.90
0.69	33.78	33.59	33.68
0.79	32.45	33.56	33.00
0.89	32.07	32.50	32.28
0.99	32.32	32.51	32.42
1.97	32.37	32.52	32.44
3.95	33.07	33.24	33.15
5.92	33.40	33.58	33.49
7.89	33.57	33.65	33.61
9.87	33.50	33.74	33.62

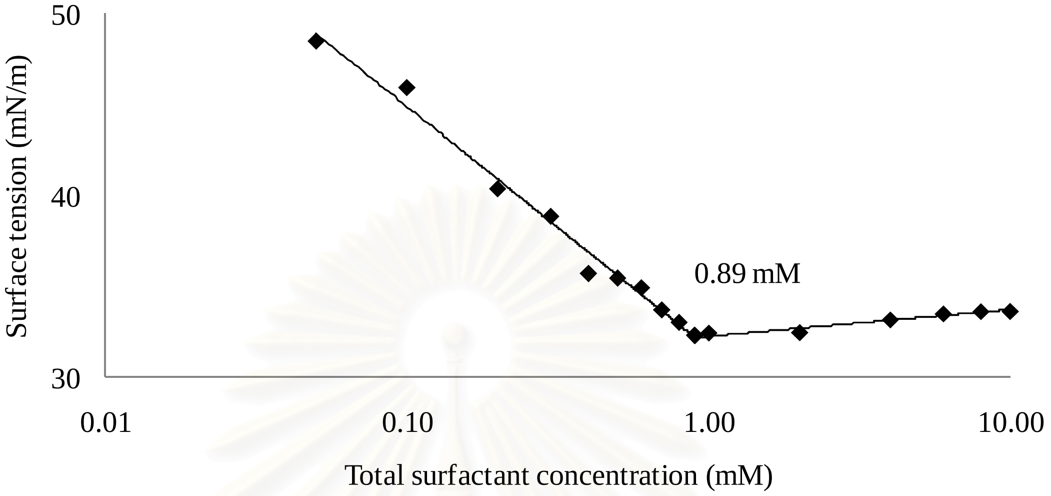

Figure B-1: CMC of the mixture Alfoterra 123-4S+AMA

Table B-2: Surface tension of Alfoterra 123-8S+AMA

Total Concentration (mM)	Surface tension 1	Surface tension 2	Average Surface Tension
0.05	41.37	42.12	41.75
0.10	37.98	38.72	38.35
0.20	34.92	35.55	35.23
0.30	32.96	33.61	33.28
0.40	33.30	33.84	33.57
0.50	33.38	33.77	33.57
0.59	33.16	33.61	33.38
0.69	33.13	33.76	33.44
0.79	33.66	33.19	33.42
0.89	33.36	33.66	33.51
0.99	33.76	33.81	33.78
1.98	33.58	33.75	33.66
3.96	33.33	33.43	33.38
5.94	33.32	33.39	33.35
7.93	33.33	33.00	33.16
9.91	33.03	33.00	33.02

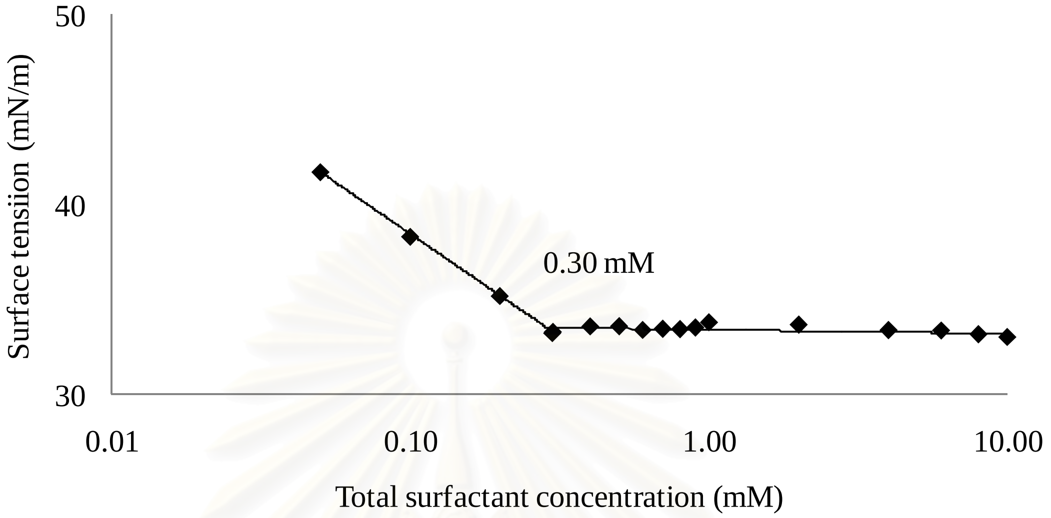

Figure B-2: CMC of the mixture Alfoterra 123-8S+AMA

Table B-3: Surface tension of Alfoterra 145-3S+AMA

Total Concentration (mM)	Surface tension 1	Surface tension 2	Average Surface Tension
0.04	48.57	47.62	48.09
0.05	45.44	45.33	45.38
0.06	43.88	43.45	43.66
0.08	42.51	42.99	42.75
0.10	41.70	42.73	42.21
0.20	37.42	37.59	37.50
0.29	36.32	36.54	36.43
0.39	34.09	34.86	34.47
0.49	33.42	34.48	33.95
0.59	33.28	33.99	33.63
0.68	32.33	33.22	32.77
0.78	33.25	33.12	33.19
0.88	33.04	33.04	33.04
0.98	33.25	33.95	33.60
1.96	33.01	32.66	32.84
3.91	32.26	32.38	32.32
5.87	32.04	31.76	31.90
7.82	31.59	31.61	31.60
9.78	31.45	31.36	31.40

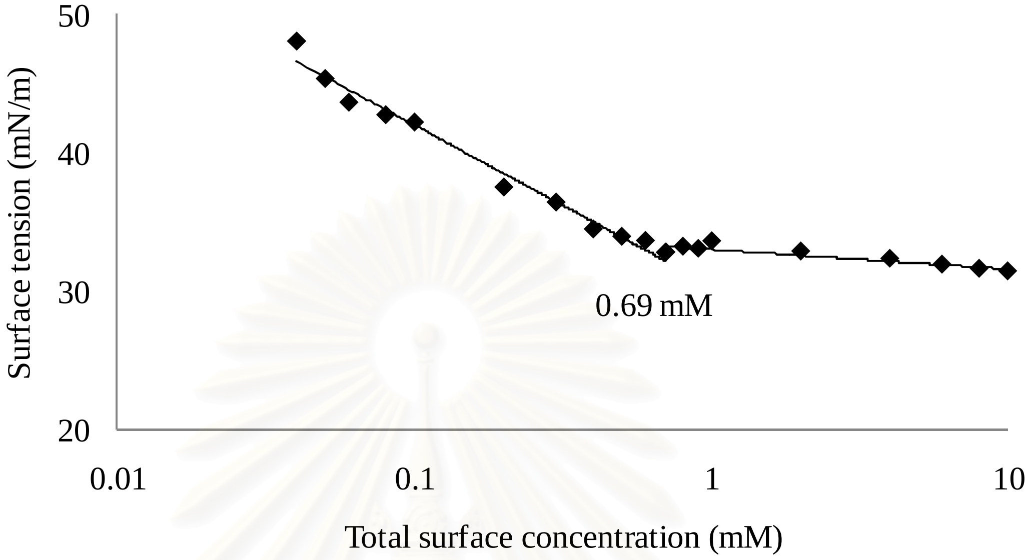

Figure B-3: CMC of the mixture Alfoterra 145-3S+AMA

Table B-4: Surface tension of Alfoterra 145-4S+AMA

Total Concentration (mM)	Surface tension 1	Surface tension 2	Average Surface Tension
0.04	46.71	47.62	47.16
0.05	41.51	40.91	41.21
0.06	40.16	41.20	40.68
0.08	38.73	38.61	38.67
0.10	37.63	37.47	37.55
0.20	35.40	35.35	35.37
0.29	33.70	32.86	33.28
0.39	33.35	33.63	33.49
0.49	33.24	33.22	33.23
0.59	32.84	33.15	32.99
0.69	33.10	33.43	33.26
0.78	32.71	32.83	32.77
0.88	32.95	33.31	33.13
0.98	32.75	33.19	32.97
1.96	32.65	32.80	32.72
3.92	32.20	32.34	32.27
5.88	31.86	32.04	31.95
7.84	31.42	31.64	31.53
9.80	31.37	31.45	31.41

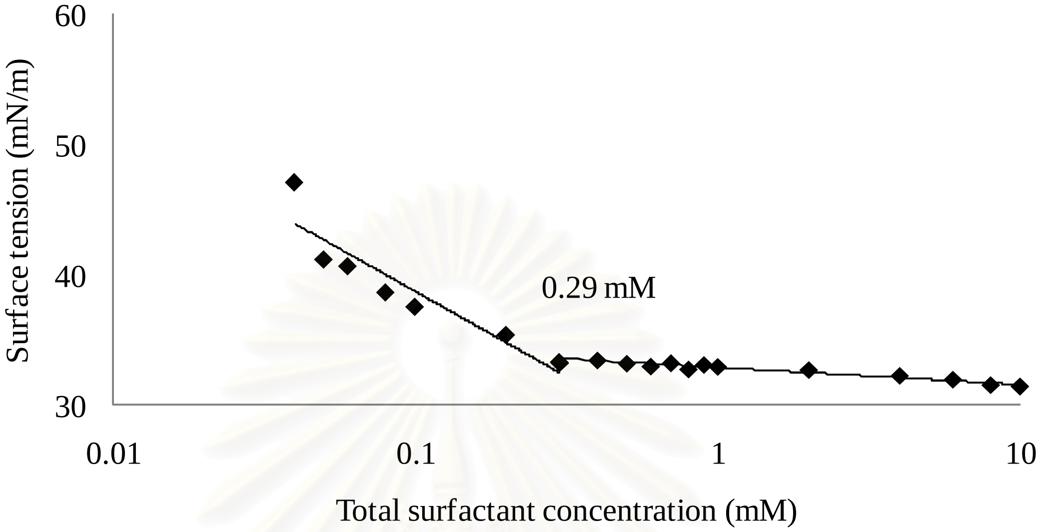

Figure B-4: CMC of the mixture Alfoterra 145-4S+AMA

Table B-5: Surface tension of Alfoterra 145-8S+AMA

Total Concentration (mM)	**Surface tension 1**	**Surface tension 2**	**Average Surface Tension**
0.02	38.63	38.18	38.40
0.04	36.96	37.94	37.45
0.05	37.92	37.27	37.59
0.06	37.08	36.91	36.99
0.08	36.22	35.84	36.03
0.10	35.75	36.48	36.11
0.20	34.59	34.16	34.37
0.30	34.39	34.85	34.62
0.39	34.10	33.83	33.97
0.49	33.61	34.54	34.08
0.59	34.09	34.05	34.07
0.69	33.54	33.78	33.66
0.79	33.91	33.13	33.52
0.89	33.73	33.22	33.47
0.99	34.10	34.36	34.23
1.97	33.28	33.69	33.48
3.94	32.95	33.14	33.05
5.92	32.65	32.68	32.66
7.89	32.53	32.48	32.50
9.86	32.32	32.35	32.33

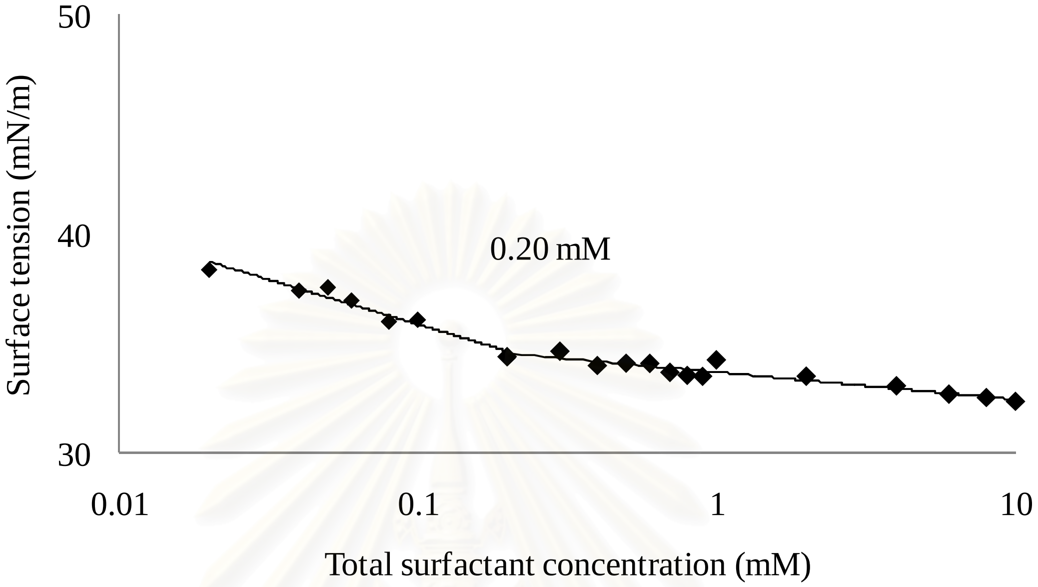

Figure B-5: CMC of the mixture Alfoterra 145-8S+AMA

Table B-6: Surface tension of Alfoterra 167-4S+AMA

Total Concentration (mM)	**Surface tension 1**	**Surface tension 2**	**Average Surface Tension**
0.01	41.93	42.62	42.28
0.02	42.13	41.23	41.68
0.03	39.82	38.97	39.40
0.04	38.70	37.86	38.28
0.05	38.35	37.74	38.05
0.06	37.12	37.89	37.51
0.07	36.56	37.23	36.90
0.08	36.12	36.84	36.48
0.09	35.17	37.77	36.47
0.10	36.00	36.65	36.33
0.19	36.00	36.86	36.43
0.29	37.61	36.75	37.18
0.39	36.81	37.50	37.16
0.49	36.89	37.42	37.15
0.58	35.65	36.35	36.00
0.68	36.95	36.93	36.94
0.78	37.18	36.12	36.65
0.88	36.12	35.53	35.83
0.97	35.85	36.85	36.35

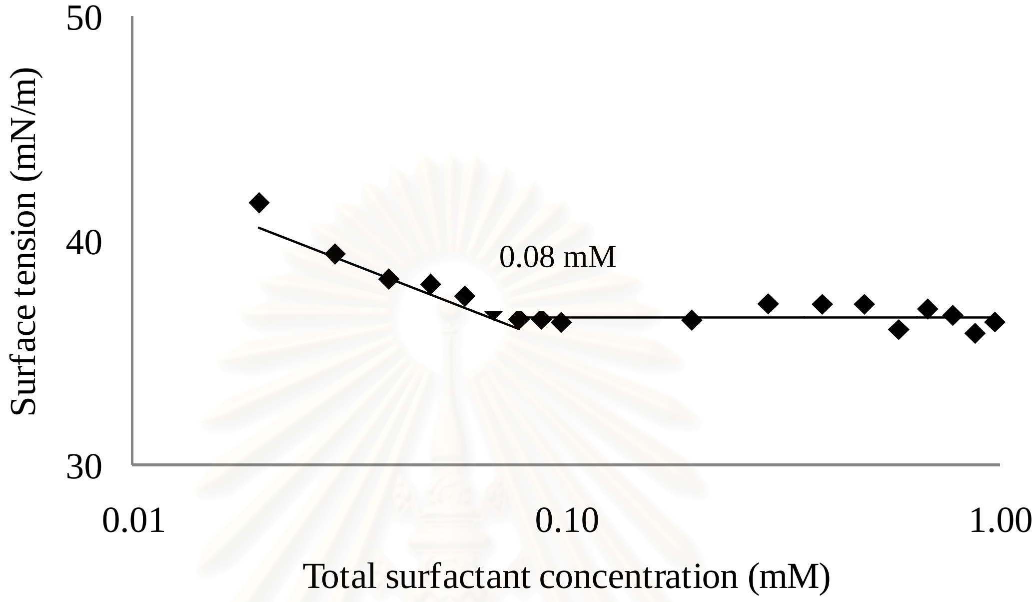

Figure B-6: CMC of the mixture Alfoterra 167-4S+AMA

Table B-7: Surface tension of Alfoterra 167-7S+AMA

Total Concentration (mM)	**Surface tension 1**	**Surface tension 2**	**Average Surface Tension**
0.01	39.91	40.25	40.08
0.02	39.76	39.60	39.68
0.03	38.66	37.67	38.16
0.04	38.51	38.45	38.48
0.05	38.65	38.70	38.68
0.06	37.37	39.00	38.18
0.07	37.44	37.68	37.56
0.08	38.53	37.04	37.79
0.09	37.07	37.36	37.21
0.10	36.98	37.33	37.16
0.20	37.33	37.43	37.38
0.29	37.48	37.25	37.37
0.39	36.70	36.67	36.68
0.49	37.86	37.14	37.50
0.59	36.95	37.29	37.12
0.69	36.95	37.22	37.09
0.78	36.38	36.61	36.49
0.88	36.52	37.41	36.97
0.98	36.38	36.94	36.66

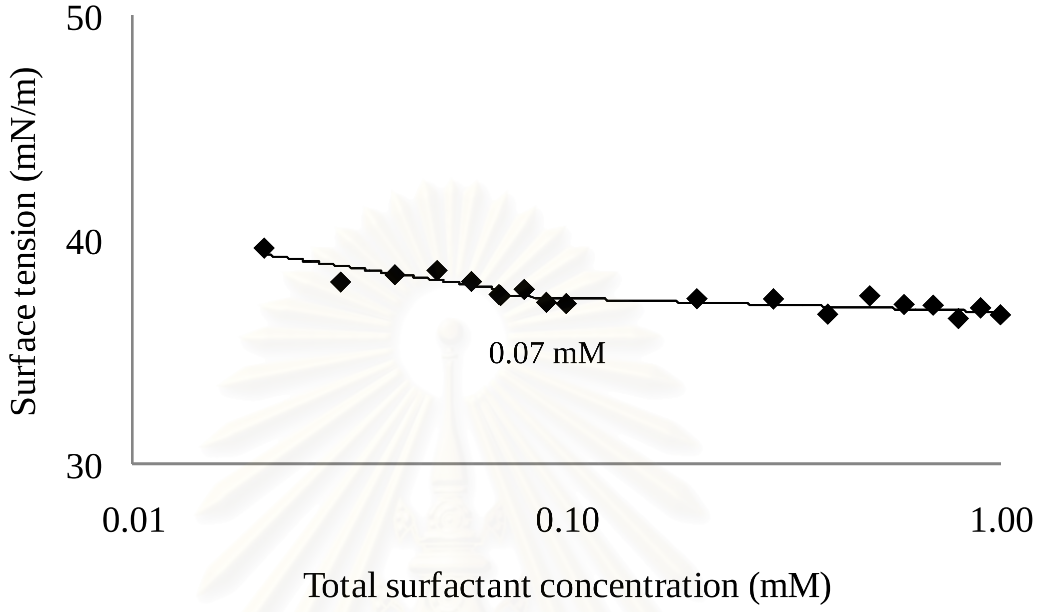

Figure B-7: CMC of the mixture Alfoterra 167-7S+AMA

Appendix C: Experimental Data of Solubilization Study

Table C-1: PCE solubility at different CMC in Alfoterra 123-4S+AMA

	Surfactant Concentration (mM)	**PCE solubility (ppm)**
minus 20CMC	0.045	313
minus 10CMC	0.09	354
CMC	0.9	538
5CMC	4.5	21,487
10CMC	9	65,130
20CMC	18	125,140
30CMC	27	163,866
40CMC	36	161,273
50CMC	45	190,349

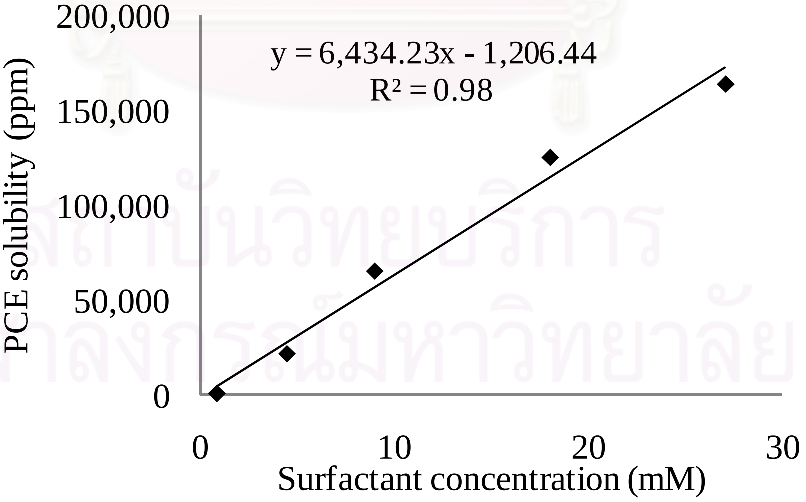

Figure C-1: MSR of the mixture Alfoterra 123-4S+AMA

Table C-2: PCE solubility at different CMC in Alfoterra 123-8S+AMA

	Surfactant Concentration (mM)	**PCE solubility (ppm)**
minus 20CMC	0.015	357
minus 10CMC	0.03	418
CMC	0.3	1,380
10CMC	3	8,864
20CMC	6	32,499
30CMC	9	55,032
40CMC	12	57,735
50CMC	15	101,968

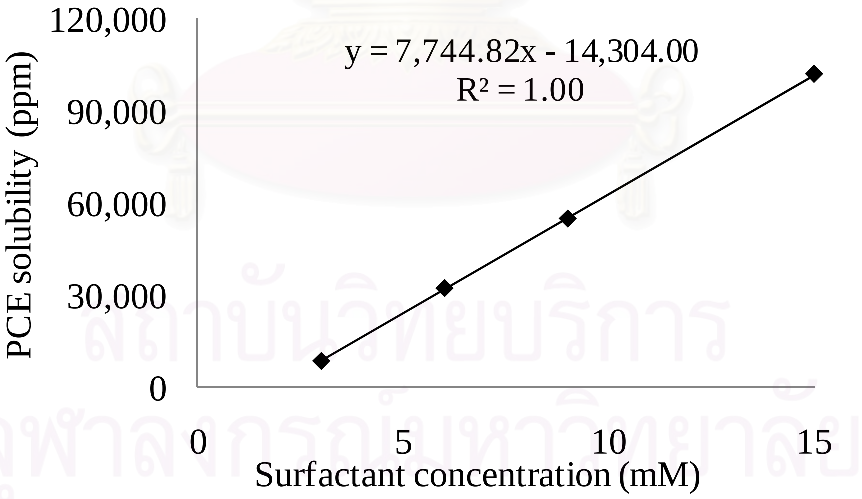

Figure C-2: MSR of the mixture Alfoterra 123-8S+AMA

Table C-3: PCE solubility at different CMC in Alfoterra 145-3S+AMA

	Surfactant Concentration (mM)	**PCE solubility (ppm)**
minus 20CMC	0.035	344
minus 10CMC	0.07	373
CMC	0.7	388
5CMC	3.5	10,822
10CMC	7	66,806
20CMC	14	121,980
30CMC	21	204,819
40CMC	28	284,302
50CMC	35	302,258

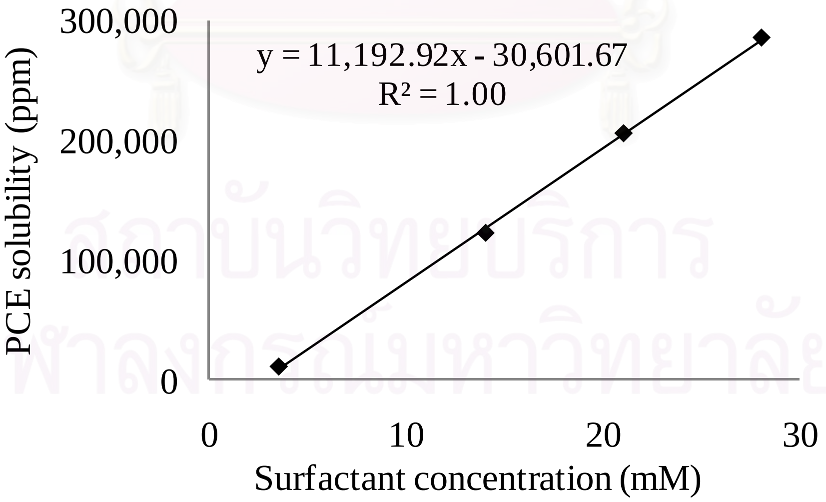

Figure C-3: MSR of the mixture Alfoterra 145-3S+AMA

Table C-4: PCE solubility at different CMC in Alfoterra 145-4S+AMA

	Surfactant Concentration (mM)	**PCE solubility (ppm)**
minus 20CMC	0.015	351
minus 10CMC	0.03	368
CMC	0.3	767
5CMC	1.5	1,094
10CMC	3	9,181
20CMC	6	35,213
30CMC	9	74,510
40CMC	12	139,491
50CMC	15	190,451

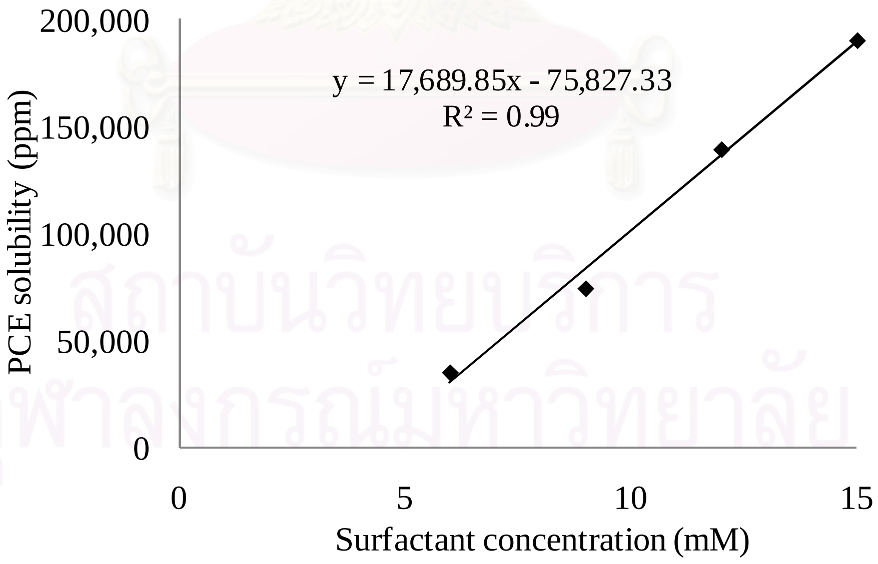

Figure C-4: MSR of the mixture Alfoterra 145-4S+AMA

Table C-5: PCE solubility at different CMC in Alfoterra 145-8S+AMA

	Surfactant Concentration (mM)	**PCE solubility (ppm)**
minus 20CMC	0.01	454
minus 10CMC	0.02	552
CMC	0.2	753
5CMC	1	2,378
10CMC	2	2,602
20CMC	4	55,084
30CMC	6	61,155
40CMC	8	124,285
50CMC	10	158,584
60CMC	12	205,612

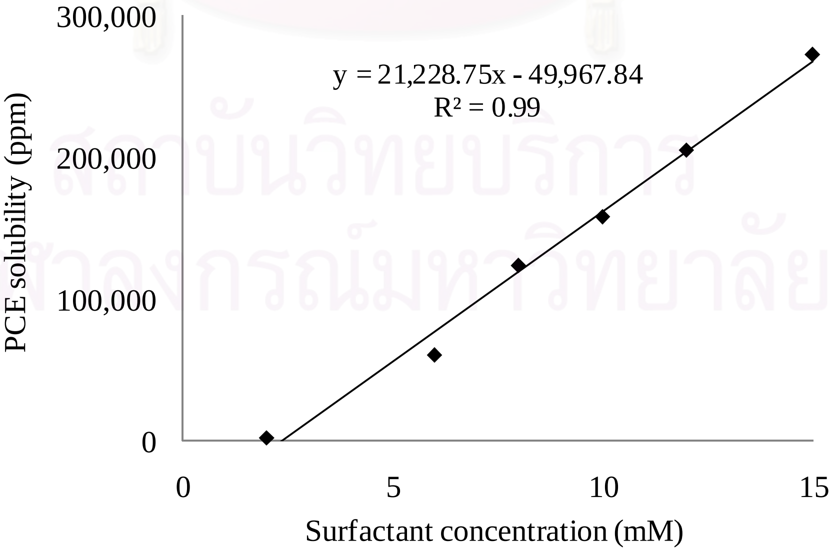

Figure C-5: MSR of the mixture Alfoterra 145-8S+AMA

Table C-6: PCE solubility at different CMC in Alfoterra 167-4S+AMA

	Surfactant Concentration (mM)	**PCE solubility (ppm)**
minus 10CMC	0.008	370
minus 5CMC	0.016	266
CMC	0.08	351
5CMC	0.4	373
10CMC	0.8	777
20CMC	1.6	863
30CMC	2.4	4,742
40CMC	3.2	8,716
50CMC	4	11,802
125CMC	10	28,964
250CMC	20	50,531

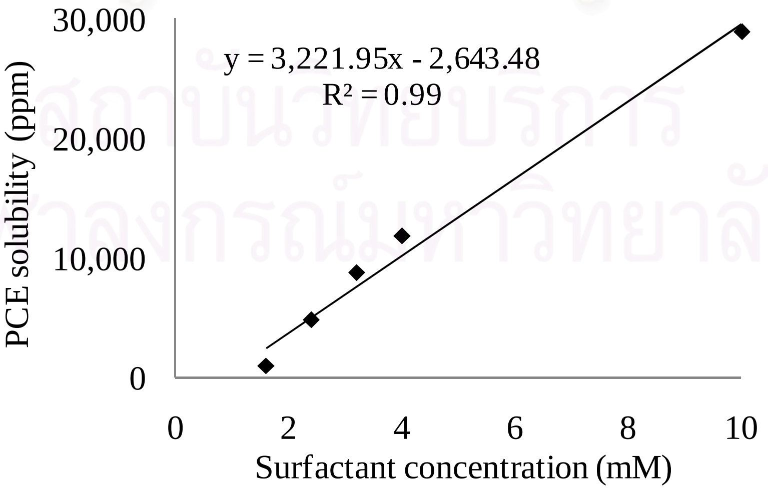

Figure C-6: MSR of the mixture Alfoterra 167-4S+AMA

Table C-7: PCE solubility at different CMC in Alfoterra 167-7S+AMA

	Surfactant Concentration (mM)	PCE solubility (ppm)
minus 10CMC	0.007	356
minus 5CMC	0.014	309
CMC	0.07	554
5CMC	0.35	765
10CMC	0.7	1,151
20CMC	1.4	1,654
30CMC	2.1	1,716
40CMC	2.8	1,712
50CMC	3.5	1,752

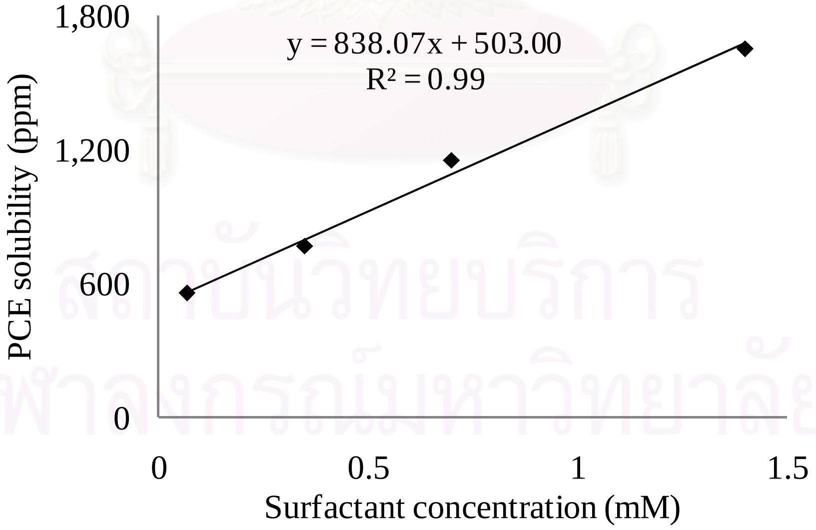

Figure C-7: MSR of the mixture Alfoterra 167-7S+AMA

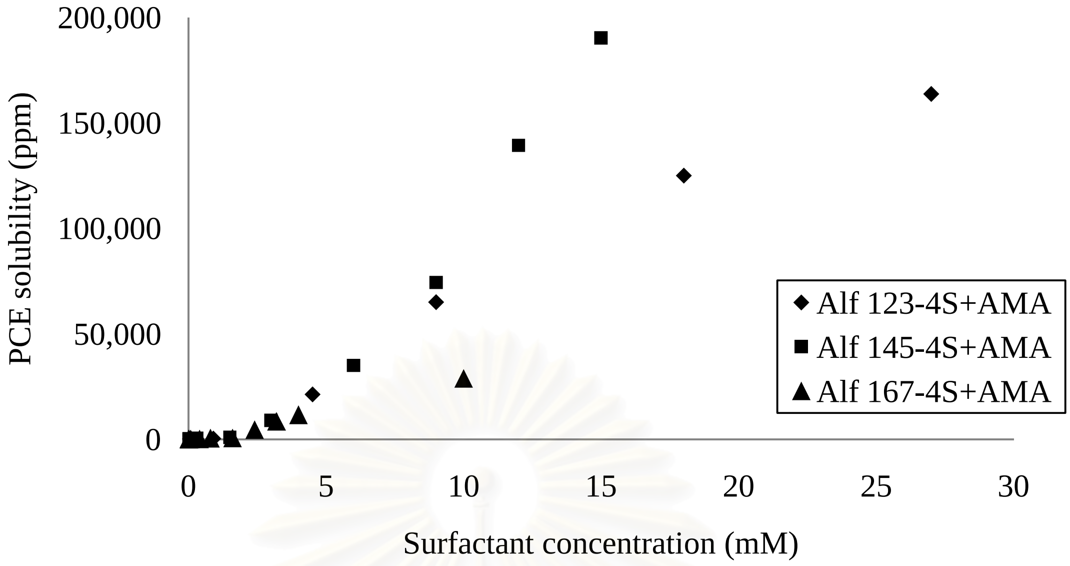

Figure C-8: MSR of each Alfoterra serie mixed with AMA at the mixing molar ratio = 1:1 at different alkyl chain length with 4 PO groups

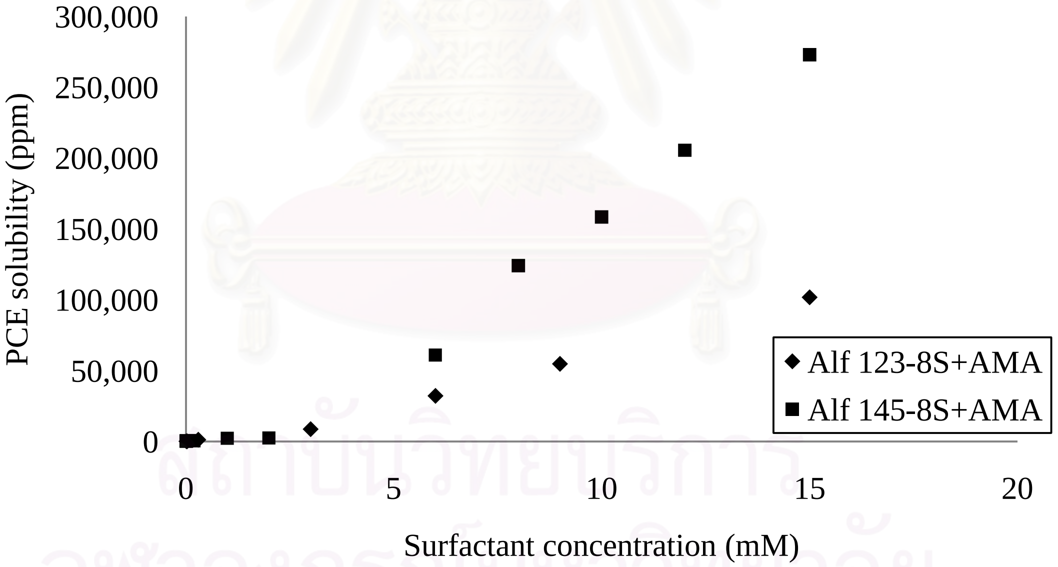

Figure C-9: MSR of each Alfoterra serie mixed with AMA at the mixing molar ratio = 1:1 at different alkyl chain length with 8 PO groups

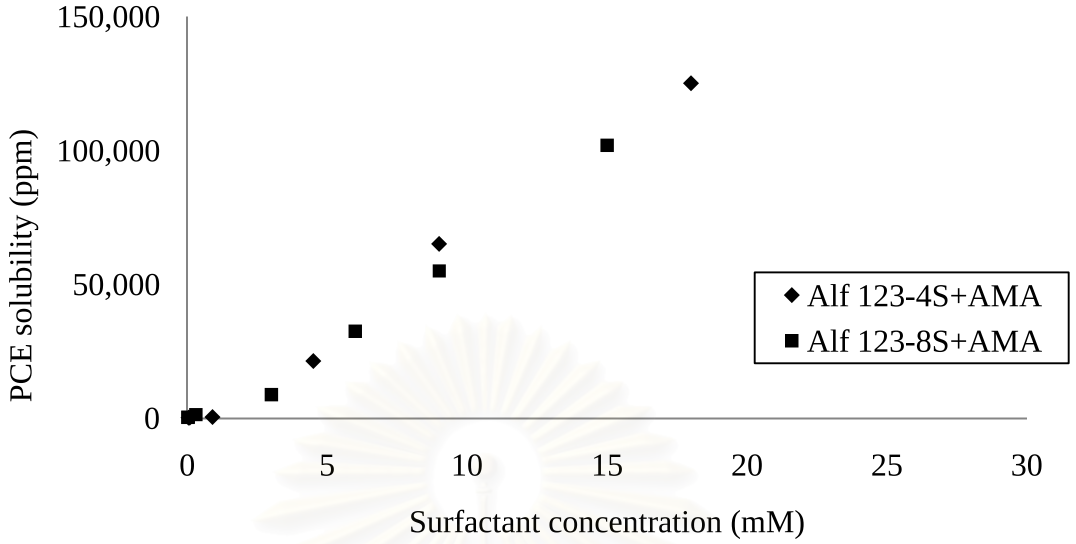

Figure C-10: MSR of each Alfoterra serie mixed with AMA at the mixing molar ratio = 1:1 at different number of PO group with C=12-13

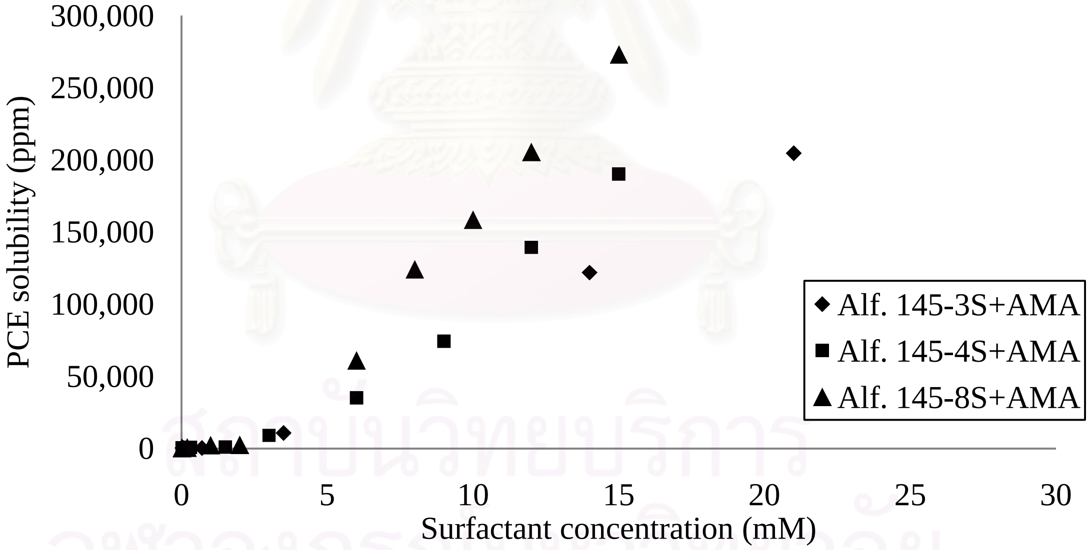

Figure C-10: MSR of each Alfoterra serie mixed with AMA at the mixing molar ratio = 1:1 at different number of PO group with C=14-15

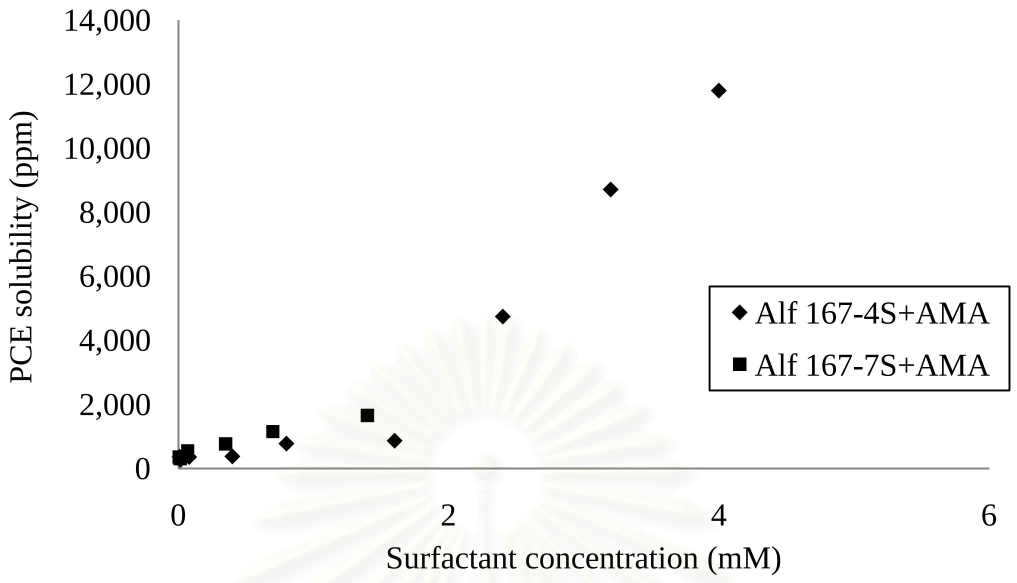

Figure C-10: MSR of each Alfoterra serie mixed with AMA at the mixing molar ratio = 1:1 at different number of PO group with C=16-17

Appendix D: Experimental Data of Column Study

Table D-1: Relationship between PCE concentration and area measured by gas chromatography couple with headspace autosample using Alfoterra 123-4S+AMA

PCE concentration (ppm)	Area	Area	Average Area	SD.	RSD.
100	646	630	638	11	1.77
300	1,730	1,824	1,777	66	3.74
500	2,785	2,707	2,746	55	2.01
800	4,329	4,618	4,474	204	4.57
1,000	7,979	8,000	7,990	15	0.19
5,000	43,260	41,742	42,501	1,073	2.53
8,000	68,137	68,076	68,107	43	0.06
10,000	82,097	83,555	82,826	1,031	1.24
30,000	206,944	206,066	206,505	621	0.30
50,000	466,856	498,852	482,854	22,625	4.69

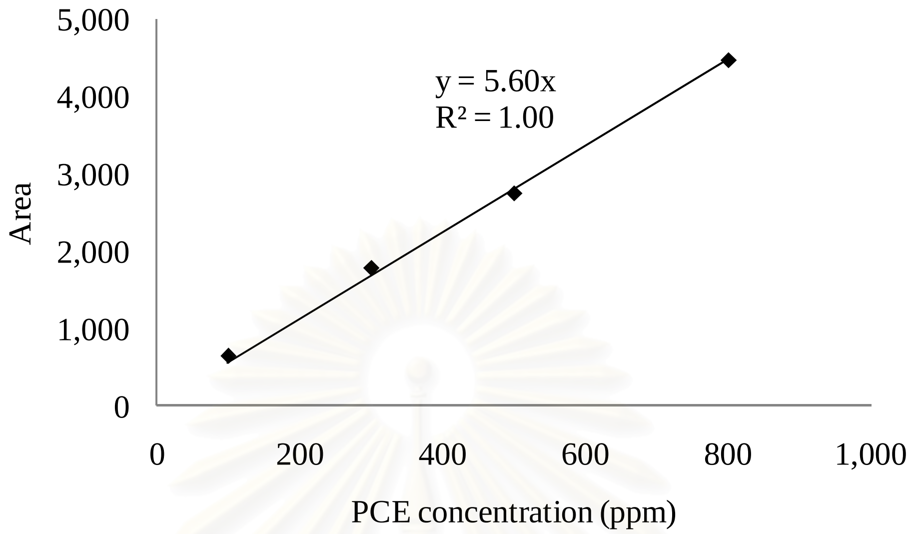

Figure D-1: Relationship between PCE concentration (100-1,000 ppm) and area measured by gas chromatography coupled with headspace auto sample using Alfoterra 123-4S+AMA

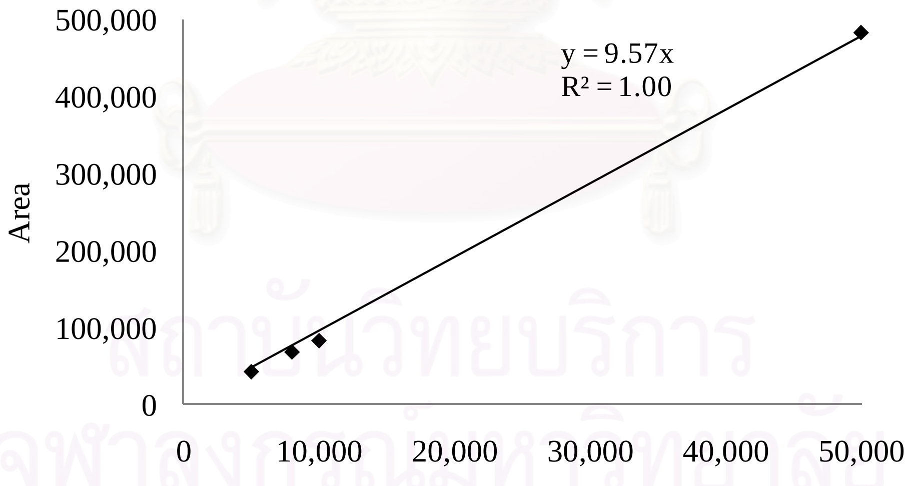

Figure D-2: Relationship between PCE concentration (5,000-50,000 ppm) and area measured by gas chromatography coupled with headspace auto sample using Alfoterra 123-4S+AMA

Table D-2: PCE concentration and accumulation at different pore volume of column study flushing with Alfoterra 123-4S+AMA

- Residual saturation (mL PCE/PV surfactant) = 15.84 ; 1 PV surfactant = 33.99 mL
- Total injected PCE = 8.72 mg

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
1	0.35	94.81	94.81	4405.30	4,405.30
2	0.71	94.66	189.47	332.60	4,737.90
3	1.06	56.37	245.85	23.30	4,761.20
4	1.41	36.02	281.87	0	4,761.20
5	1.77	12.60	294.47	0	4,761.20
6	2.12	10.84	305.31	0	4,761.20
7	2.47	8.85	314.15	0	4,761.20
8	2.82	10.82	324.97	0	4,761.20
9	3.18	10.46	335.44	0	4,761.20
10	3.53	10.87	346.30	0	4,761.20
11	3.88	7.30	353.60	0	4,761.20
12	4.24	6.30	359.90	0	4,761.20
13	4.59	5.83	365.73	0	4,761.20
14	4.94	4.89	370.62	0	4,761.20
15	5.30	4.99	375.62	0	4,761.20
16	5.65	4.71	380.33	0	4,761.20
17	6.00	4.28	384.61	0	4,761.20
18	6.35	2.18	386.79	0	4,761.20
19	6.71	2.86	389.65	0	4,761.20

Table D-2 (continue).

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
20	7.06	2.54	392.18	0	4,761.20
21	7.41	1.04	393.23	0	4,761.20
22	7.77	0.51	393.74	0	4,761.20
23	8.12	0.56	394.30	0	4,761.20
24	8.47	0.63	394.93	0	4,761.20
25	8.83	0.53	395.46	0	4,761.20
26	9.18	0.43	395.90	0	4,761.20
27	9.53	0.32	396.22	0	4,761.20
28	9.89	0.27	396.48	0	4,761.20
29	10.24	0.25	396.73	0	4,761.20
30	10.59	0.16	396.90	0	4,761.20
31	10.94	0.15	397.04	0	4,761.20
32	11.30	0.11	397.15	0	4,761.20
33	11.65	0.12	397.27	0	4,761.20
34	12.00	0.09	397.35	0	4,761.20
35	12.36	0.08	397.44	0	4,761.20
36	12.71	0.05	397.49	0	4,761.20
37	13.06	0.04	397.54	0	4,761.20
38	13.42	0.04	397.57	0	4,761.20
39	13.77	0.04	397.61	0	4,761.20
40	14.12	0.03	397.64	0	4,761.20
41	14.47	0.04	397.68	0	4,761.20

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
42	14.83	0.03	397.72	0	4,761.20

Residual saturation = (volume of PCE in column/pore volume) x 100

Table D-3: Relationship between PCE concentration and area measured by gas chromatography couple with headspace autosample using Alfoterra 145-4S+AMA

PCE concentration (ppm)	Area	Area	Average Area	SD.	RSD.
100	712	725	18	2.54	725
300	2,113	2,095	25	1.22	2,095
500	2,982	3,022	56	1.85	3,022
800	4,763	4,676	123	2.63	4,676
1,000	6,258	6,182	107	1.74	6,182
5,000	35,234	36,142	35,688	642	0.02
8,000	57,142	57,738	57,440	421	0.01
10,000	71,011	70,914	70,963	69	0.00
30,000	277,514	284,389	280,952	4,861	0.02
50,000	1,351,392	1,296,182	1,323,787	39,039	0.03

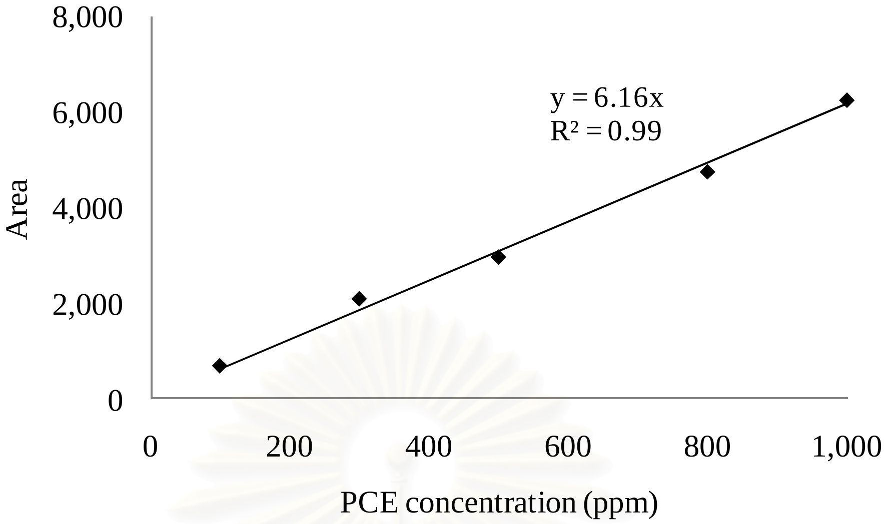

Figure D-3: Relationship between PCE concentration (100-1,000 ppm) and area measured by gas chromatography coupled with headspace auto sample using Alfoterra 145-4S+AMA

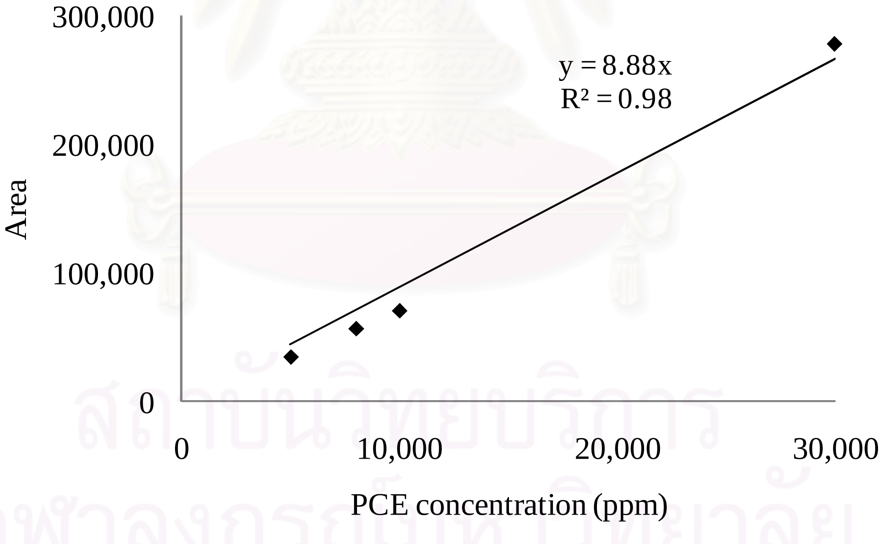

Figure D-4: Relationship between PCE concentration (5,000-30,000 ppm) and area measured by gas chromatography coupled with headspace auto sample using Alfoterra 145-4S+AMA

Table D-4: PCE concentration and accumulation at different pore volume of column study flushing with Alfoterra 145-4S+AMA

- Residual saturation (mL PCE/PV surfactant) = 15.10 ; 1 PV surfactant = 32.85 mL
- Total injected PCE = 8.04 mg

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
1	0.40	154.91	154.91	3,480.80	3,480.80
2	0.79	285.89	440.80	2,009.10	5,489.90
3	1.19	260.58	701.37	10.80	5,500.70
4	0.40	107.32	808.70	0	5,500.70
5	0.79	68.63	877.32	0	5,500.70
6	1.19	34.76	912.09	0	5,500.70
7	0.40	17.04	929.13	0	5,500.70
8	0.79	17.04	946.17	0	5,500.70
9	1.19	16.13	962.30	0	5,500.70
10	0.40	15.94	978.25	0	5,500.70
11	0.79	15.42	993.67	0	5,500.70
12	1.19	14.24	1,007.91	0	5,500.70
13	0.40	12.85	1,020.77	0	5,500.70
14	0.79	13.88	1,034.65	0	5,500.70
15	1.19	12.78	1,047.43	0	5,500.70
16	0.40	11.28	1,058.71	0	5,500.70
17	0.79	11.10	1,069.82	0	5,500.70
18	1.19	10.77	1,080.59	0	5,500.70
19	0.40	9.84	1,090.43	0	5,500.70

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
20	0.79	10.79	1,101.22	0	5,500.70
21	1.58	6.97	1,108.19	0	5,500.70
22	1.98	7.02	1,115.21	0	5,500.70
23	2.37	6.56	1,121.77	0	5,500.70
24	2.77	5.30	1,127.07	0	5,500.70
25	3.16	6.33	1,133.40	0	5,500.70
26	3.56	6.00	1,139.40	0	5,500.70
27	3.95	5.45	1,144.85	0	5,500.70
28	4.35	5.24	1,150.10	0	5,500.70
29	4.75	4.39	1,154.49	0	5,500.70
30	5.14	4.58	1,159.07	0	5,500.70
31	5.54	4.93	1,164.01	0	5,500.70
32	5.93	4.92	1,168.92	0	5,500.70
33	6.33	5.02	1,173.94	0	5,500.70
34	6.72	4.75	1,178.69	0	5,500.70
35	7.12	5.03	1,183.72	0	5,500.70
36	7.51	5.06	1,188.78	0	5,500.70
37	7.91	4.82	1,193.60	0	5,500.70
38	8.30	4.47	1,198.07	0	5,500.70
39	8.70	4.13	1,202.19	0	5,500.70
40	9.09	4.47	1,206.67	0	5,500.70
41	9.49	4.15	1,210.81	0	5,500.70

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
42	9.89	4.06	1,214.87	0	5,500.70
43	10.28	3.45	1,218.32	0	5,500.70
44	17.40	3.97	1,222.29	0	5,500.70
45	17.79	3.70	1,225.99	0	5,500.70
46	18.19	3.24	1,229.23	0	5,500.70
47	18.59	3.08	1,232.31	0	5,500.70
48	18.98	2.55	1,234.86	0	5,500.70
49	19.38	2.22	1,237.08	0	5,500.70
50	19.77	2.31	1,239.39	0	5,500.70
51	20.17	2.33	1,241.72	0	5,500.70
52	20.56	2.12	1,243.84	0	5,500.70
53	20.96	1.92	1,245.76	0	5,500.70
54	21.35	1.60	1,247.36	0	5,500.70
55	21.75	1.66	1,249.02	0	5,500.70
56	22.14	1.41	1,250.42	0	5,500.70
57	22.54	1.34	1,251.76	0	5,500.70
58	22.94	1.31	1,253.07	0	5,500.70
59	23.33	1.30	1,254.37	0	5,500.70
60	23.73	1.24	1,255.61	0	5,500.70
61	24.12	1.20	1,256.82	0	5,500.70

Table D-4: Relationship between PCE concentration and area measured by gas chromatography couple with headspace autosample using Alfoterra 145-8S+AMA

PCE concentration (ppm)	Area	Area	Average Area	SD.	RSD.
100	656	571	614	60.10	9.80
300	1,949	2,050	2,000	71.42	3.57
500	3,095	3,338	3,217	171.83	5.34
800	5,625	5,500	5,563	88.39	1.59
1,000	6,693	6,748	6,721	38.89	0.58
5,000	35,193	36,217	35,705	724	2.03
8,000	59,356	59,801	59,579	315	0.53
10,000	75,267	75,266	75,267	1	0.00
30,000	240,591	233,193	236,892	5,231	2.21
50,000	379,396	345,945	362,671	23,653	6.52

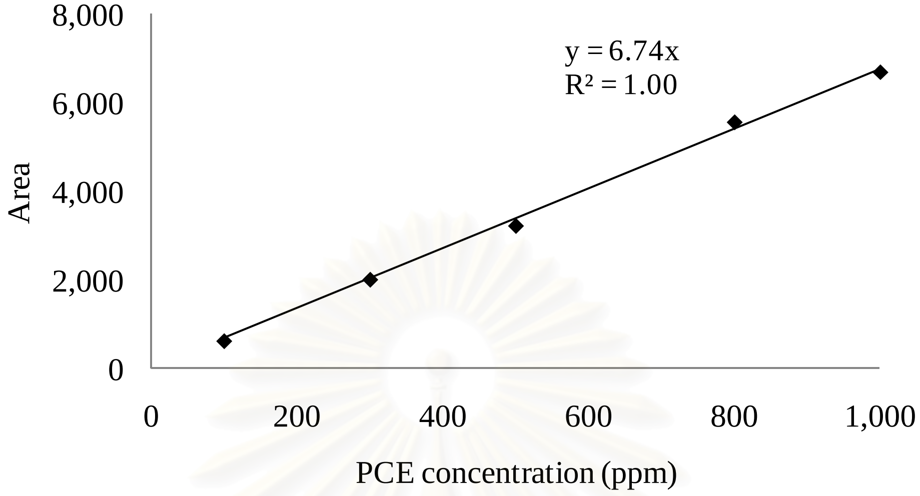

Figure D-5: Relationship between PCE concentration (100-1,000 ppm) and area measured by gas chromatography coupled with headspace auto sample using Alfoterra 145-8S+AMA

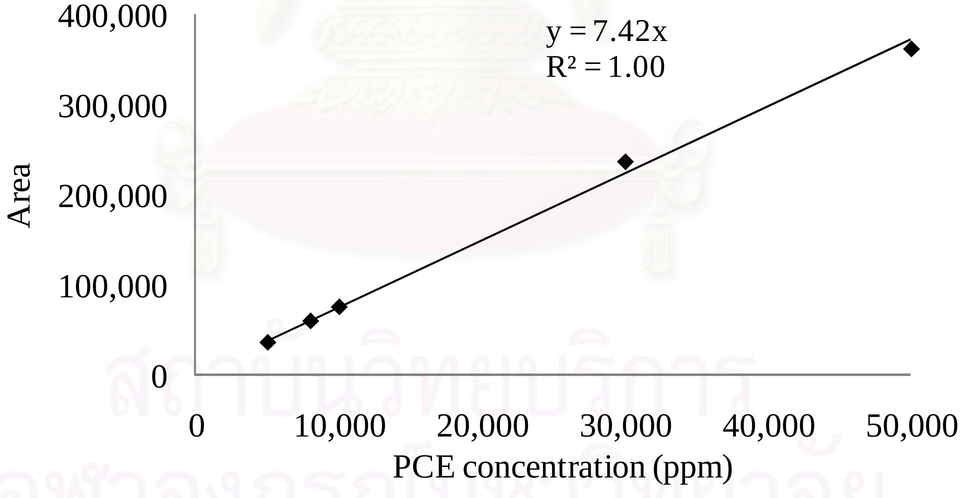

Figure D-6: Relationship between PCE concentration (5,000-30,000 ppm) and area measured by gas chromatography coupled with headspace auto sample using Alfoterra 145-8S+AMA

Table D-6: PCE concentration and accumulation at different pore volume of column study flushing with Alfoterra 145-8S+AMA

- Residual saturation (mL PCE/PV surfactant) = 15.23 ; 1 PV surfactant = 33.15 mL
- Total injected PCE = 8.18 mg

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
1	0.36	76.31	76.31	1,245.80	1,245.80
2	0.72	235.62	311.94	305.80	1,551.60
3	1.09	243.64	555.58	95.80	1,647.40
4	1.45	247.83	803.41	55.40	1,702.80
5	1.81	292.72	1,096.13	34.70	1,737.50
6	2.17	303.32	1,399.45	148.80	1,886.30
7	2.53	314.37	1,713.82	0	1,886.30
8	2.90	276.45	1,990.27	0	1,886.30
9	3.26	293.74	2,284.02	0	1,886.30
10	3.62	250.44	2,534.45	0	1,886.30
11	3.98	229.50	2,763.95	0	1,886.30
12	4.34	196.01	2,959.96	0	1,886.30
13	4.71	188.51	3,148.47	0	1,886.30
14	5.07	176.13	3,324.60	0	1,886.30
15	5.43	165.77	3,490.37	0	1,886.30
16	5.79	159.62	3,649.99	0	1,886.30
17	6.15	148.71	3,798.70	0	1,886.30
18	6.52	140.74	3,939.44	0	1,886.30
19	6.88	135.16	4,074.60	0	1,886.30

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
20	7.24	119.78	4,194.38	0	1,886.30
21	7.60	96.80	4,398.92	0	1,886.30
22	7.96	85.59	4,484.51	0	1,886.30
23	8.33	72.85	4,557.35	0	1,886.30
24	8.69	63.64	4,620.99	0	1,886.30
25	9.05	52.22	4,673.21	0	1,886.30
26	9.41	42.67	4,715.88	0	1,886.30
27	9.77	35.92	4,751.80	0	1,886.30
28	10.14	27.51	4,779.31	0	1,886.30
29	10.50	24.15	4,803.45	0	1,886.30
30	10.86	19.16	4,822.61	0	1,886.30
31	11.22	16.30	4,838.91	0	1,886.30
32	11.58	14.60	4,853.51	0	1,886.30
33	11.95	12.50	4,866.01	0	1,886.30
34	12.31	10.19	4,876.19	0	1,886.30
35	12.67	8.31	4,884.50	0	1,886.30
36	13.03	6.70	4,891.20	0	1,886.30
37	13.39	4.99	4,896.19	0	1,886.30
38	13.76	5.56	4,901.76	0	1,886.30
39	14.12	4.57	4,906.32	0	1,886.30
40	14.48	3.14	4,909.46	0	1,886.30
41	14.84	2.65	4,912.11	0	1,886.30

No.	PV	PCE solubilization (mg)	PCE solubilization accumulation (mg)	PCE mobilization (mg)	PCE mobilization accumulation (mg)
42	15.20	2.82	4,914.92	0	1,886.30
43	15.57	96.80	4,398.92	0	1,886.30
44	15.93	2.08	4,917.00	0	1,886.30
45	16.29	1.62	4,918.62	0	1,886.30
46	16.65	1.42	4,920.04	0	1,886.30
47	17.01	1.05	4,921.09	0	1,886.30
48	17.38	0.79	4,921.88	0	1,886.30
49	17.74	0.80	4,922.69	0	1,886.30
50	18.10	0.12	4,922.81	0	1,886.30
51	18.46	0.12	4,922.93	0	1,886.30
52	18.82	0.11	4,923.04	0	1,886.30
53	19.19	0.09	4,923.13	0	1,886.30
54	19.55	0.09	4,923.22	0	1,886.30
55	19.91	0.09	4,923.31	0	1,886.30
56	20.27	0.09	4,923.40	0	1,886.30

BIOGRAPHY

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- Jirussavadee Aumpuch, Punjaporn Weschayanwiwat, and Chantra Tongcumpou. *Enhanced Tetrachloroethylene Solubilization by Extended Surfactant*. 1st The Proceedings of Pure and Applied Chemistry International Conference (PACCON) 2008, Bangkok, Thailand, January 30 - February 1, 2008. Organized by Kasetsart University, Chemical Society of Thailand, and The Thailand Research Fund.

- Jirussavadee Aumpuch, Punjaporn Weschayanwiwat, and Chantra Tongcumpou. *Removal of tetrachloroethylene by extended surfactants flushing in column study*. The 2008 International conference on Environmental Quality Concern, Control and Conservation (EQC 2008), Tainan, Taiwan, May 23-24, 2008. Organized by Chia Nan University of Pharmacy and Science, Taiwan Chung-Hwa University of Medical Technology, Taiwan Tajen University, Taiwan King Mongkut's University of Technology Thonburi, Thailand, and National Center of Excellence for Environmental and Hazardous Waste Management, Thailand.